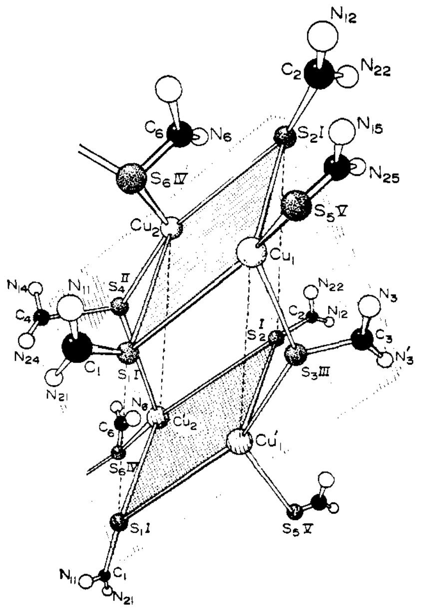


Figure 1. Perspective view of the $Cu_4(tu)_9(NO_3)_4$ polymer. S_6 at the top left bridges this "tetramer" to an adjacent "tetramer" to complete the polymer; see also S_6 at lower right. Dotted area indicates the approximate plane defined by Cu_1,Cu_2,S_1,S_2.

with a C–S σ and π bond and the nonbonding electron pairs in sp^2 orbitals in the molecular plane, then the above analogies, items 3 and 4, are all understandable by considering the four-membered ring as two sets of three-center electron-deficient bonds. Each Cu contributes a $\sigma(sp^3)$ orbital and each S one sp^2 orbital with its electron pair to this three-center bridge.[9] This is equivalent to a four-center, four-electron, electron-deficient description. The average S–C distance, 1.75 A, is only slightly greater than one standard deviation (±0.03 A) of the 1.71 ± 0.01 A observed in free thiourea.[10] In contrast to the Ag–S–Ag bridge in $Ag(tu)_2Cl$, this type of electron-deficient bridge does not require a lengthening of the S–C bond. Hence, there is no demand for the use of the Cu 3d orbitals as was true of the 4d orbitals in $Ag(tu)_2Cl$.

The Cu_2–S_4–Cu_2' bridge (type II) also appears to be electron deficient (using one sp^2 S orbital with its electron pair and two empty Cu orbitals), since the entire thiourea group must be in the mirror plane relating the Cu_2 to Cu_2' and the angle between S_4–(Cu_2–Cu_2' bisector) and the S_4–C_4 bond is 112°. However, since the Cu_2–Cu_2' distance is 4.192 ± 0.005 A and the Cu_2–S_4–Cu_2' angle is 122.0 ± 0.2°, this bridge must be much weaker and more complicated than the type I bridges.

The Cu_1–S_3–Cu_1' bridge (type III) is probably, in terms of bonding, the most complicated. In contrast to the Cu_2–S_4–Cu_2' bridge, only the S_3–C_3 bond of the thiourea group lies in the crystallographic mirror relating Cu_1 to Cu_1' and N_3 to N_3'. The distance between Cu_1 and Cu_1' is 4.161 ± 0.005 A, and the Cu_1–S_3–Cu_1' angle is 123.2 ± 0.2°. Further, the dihedral angle between the S_3 thiourea plane and the Cu_1–S_3–Cu_1' plane is 128°. This probably means that the sulfur $p\pi$MO as well as the sp^2 nonbonding orbitals both contribute electrons to this bridge, and even d orbitals may be involved.

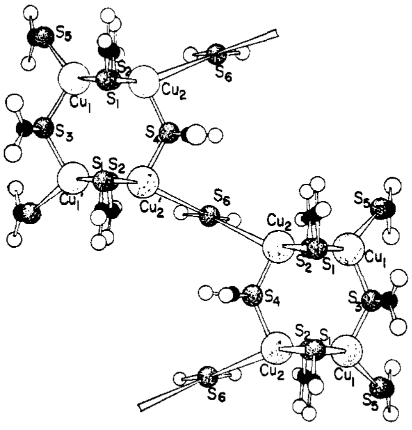


Figure 2. A side view of the $Cu_4(tu)_9(NO_3)_4$ polymer. A crystallographic mirror plane passes through S_4 and its thiourea group but only through S_3 and its associated carbon atom. The orientation of the S_1 and S_2 thiourea groups is noteworthy.

The S_6 bridging group connects two Cu atoms by more or less normal electron-pair bonds using both electron pairs in the sulfur sp^2 orbitals. S_5 is nonbridging and donates one electron pair from one of its sp^2 nonbonding orbitals to Cu_1. Hence we have five different types of metal–sulfur bonds, at least one of which is a completely new type of electron-deficient bond.

Acknowledgment. This research was supported by National Institutes of Health Grants GM 0833-03,04 and GM 13985-01.

---

[9] Diagramatically, this description is the same as ref 1, Figure 2, with $\psi ED = \sigma_1 + \sigma_2 + sp^2$. Other changes are obvious.

[10] N. R. Kunchur and M. R. Truter, *J. Chem. Soc.*, 2551 (1958).

(11) In partial fulfillment of the Ph.D. requirements, University of Pittsburgh, 1966.

(12) Address all correspondence to this author.

R. G. Vranka,[11] **E. L. Amma**[12]
Department of Chemistry, University of South Carolina
Columbia, South Carolina 29208

Received June 13, 1966

The Replacement of Phenolic Hydroxyl Groups by Hydrogen

Sir:

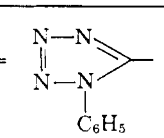
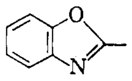
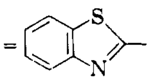
Up to the present time, no general method has been available for the removal of phenolic hydroxyl groups.[1] A method has recently been reported[2] for removing the phenolic hydroxyl group of various 3-methoxy-4-hydroxymorphine derivatives. This method involves a sodium and liquid ammonia cleavage of phenol ethers, whereas a similar, more generally applicable procedure[1] requires the preparation of a 2,4-dinitrophenyl ether of the phenol and catalytic reduction to the unstable diaminophenyl ether, followed by a sodium and liquid ammonia cleavage of the substituted ether to effect the desired replacement of phenolic hydroxyl group by hydrogen. Both of these procedures are based on the cleavage of diphenyl ethers by sodium in liquid ammonia,

---

(1) W. H. Pirkle and J. L. Zabriskie, *J. Org. Chem.*, **29**, 3124 (1964), and references cited therein.

(2) Y. K. Sawa, N. Tsuji, and S. Maeda, *Tetrahedron*, **15**, 144, 154 (1961); Y. K. Sawa, N. Tsuji, K. Okabe, and T. Miyamono, *ibid.*, **21**, 1121 (1965); Y. K. Sawa and J. Irisawa, *ibid.*, **21**, 1129 (1965); Y. K. Sawa, M. Horiuchi, and K. Tanaka, *ibid.*, **21**, 1133 (1965).

Table I. Hydrogenolysis of Phenolic Ethers

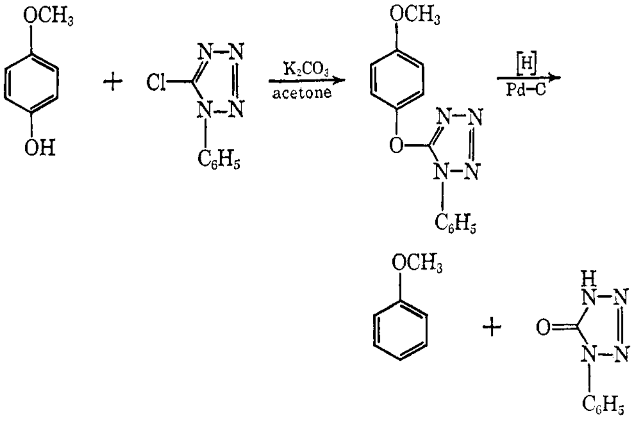
R =

R′ =

R′′ =


Parent phenol	Heterocyclic ether[a,b]	Ether yield, %	Ether mp, °C	Hydrogenolysis time, hr[e]	% yield[e] Aromatic product	% yield[e] Hydroxy-heterocycle
Guaiacol	R	94	111–112	15	86,[f] anisole	70
Guaiacol	R′′	78[c]	66–67	16	0[f]	0
m-Methoxyphenol	R	95	87–88	16	85,[f] anisole	54
p-Methoxyphenol	R	97	81–82	6	83,[f] anisole	70
o-Phenylphenol	R	98	112–113	8	82, biphenyl	82
o-Phenylphenol	R′	86	66–67	15	82, biphenyl	85
p-Phenylphenol	R	93	152–153	7	78, biphenyl	82
				15	78,[g] biphenyl	89
p-Phenylphenol	R′	98	116–117	16	75, biphenyl	92
p-Phenylphenol	R′′	83[d]	106–107	16	0[j]	. .
p-Aminophenol	R	86	171–173	9	46,[h] aniline	73
p-Carbethoxyphenol	R	91	88–89	4	63,[f] ethylbenzoate	60
				16	89,[f] ethylbenzoate	46
Thymol	R	93	77–78	9	35,[f] *p*-cymene	33
				15	72,[f] *p*-cymene	47
1-Naphthol	R	88	108–109	7	50, naphthalene	82
2-Naphthol	R	94	136–137	17	65, naphthalene	94
p-Chlorophenol	R	92	94–95	18	70,[f,g,i] benzene	77

[a] Prepared by heating at reflux overnight equimolar quantities of phenol and chloroheterocycle in dry acetone with a twofold excess of anhydrous potassium carbonate. [b] Satisfactory analyses were obtained for all new compounds. [c] Refluxed for 6 days. [d] Refluxed for 3 days. [e] Hydrogenolyses run in benzene at 35°; isolated yields unless otherwise noted. [f] Filtered solution analyzed directly by vpc with toluene as an internal standard. [g] Ethanol solvent. [h] Isolated as the hydrochloride. [i] Hydrogenolysis of the carbon–chlorine bond occurred. Both hydrogenolysis reactions failed to proceed under identical conditions when benzene was used as solvent. [j] 2-Chlorobenzothiazole was also used to prepare several heterocyclic ethers. However, with as much as 80% catalyst under the usual conditions, none of the desired hydrogenolysis products were obtained. The only base-soluble material isolated, when reduction of the benzothiazolyl ether of *p*-phenylphenol was attempted with 60% by weight palladium on charcoal, was *p*-phenylphenol in 11% yield. Again, hydrogenolysis occurred in the undesired manner.

a reaction studied earlier by Sowa and co-workers[3a] and more recently by Tomita and co-workers[3b] and by Strojny.[3c] The useful scope of these reactions is apparently limited to phenols with *o*-methoxy or -aryl substituents.[1]

A mild method for the removal of phenolic hydroxyl groups has been discovered which appears to be quite general. The new procedure consists in preparing an ether of the phenolic hydroxyl with certain heterocyclic compounds and then subjecting this ether to catalytic hydrogenolysis over 5% palladium on charcoal to cleave the heterocyclic ether group. The reaction sequence is illustrated for the case of *p*-methoxyphenol, which produces anisole in good yield. The heterooxy ethers are easily prepared in high yield as crystalline solids when 2-chlorobenzoxazole and 1-phenyl-5-chlorotetrazole[4] are employed (see Table I). The hydrogenolysis reaction proceeds readily in a Parr shaker at 35° in benzene, ethanol, or tetrahydrofuran with palladium on charcoal (see Table I). Platinum oxide catalyst can also be used; anisole was obtained in 67% yield from the phenyltetrazolyl ether of guaiacol under the same conditions. Phenolic hydroxyl groups could not be removed with Raney nickel catalyst. In fact, when the reduction of the phenyltetrazolyl ether of *p*-phenylphenol was attempted with Raney nickel, *p*-phenylphenol was obtained in 4% yield; hydrogenolysis occurred in the undesired sense to regenerate the starting phenol.



Of the heterocyclic ethers examined, the phenyltetrazolyl ethers appear most advantageous for the hydrogenolysis reaction. Not only do they afford the highest melting, most readily formed ethers, but they and the 1-phenyl-5-tetrazolone formed have the least poisoning effect on the palladium catalyst. Thus, whereas it was found that 10 to 20% by weight of catalyst worked well for the cleavage of tetrazolyl ethers, the use of 20% and preferably as much as 40% catalyst was necessary to obtain satisfactory reduction with benzoxazolyl ethers.[5]

The procedure is quite general, as shown in Table I, and produces the desired dehydroxylated materials in good yields. Application of the method of sodium and liquid ammonia cleavage of the reduced dinitrophenyl

---

(3) (a) P. A. Sartoretto and F. J. Sowa, *J. Am. Chem. Soc.*, **59**, 603 (1937); A. L. Kranzfelder, J. J. Verbanc, and F. J. Sowa, *ibid.*, **59**, 1488 (1937); F. C. Weber and F. J. Sowa, *ibid.*, **60**, 94 (1938). (b) For the last of many articles, see M. Tomita, H. Furukawa, S. T. Lu, and S. Morris, *Tetrahedron Letters*, 4309 (1965). (c) E. J. Strojny, *J. Org. Chem.*, **31**, 1662 (1966).

(4) C. A. Maggiulli and R. A. Paine, Belgian Patent 671,402 (1966).

(5) See footnote *j*, Table I.

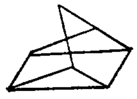
ethers[1] of the isomeric methoxy phenols gave anisole from *o*-, *m*-, and *p*-methoxyphenol in 60, 31, and 0% yields, respectively. The method described here for the 1-phenyl-5-tetrazolyl ethers gave anisole in over 80% yields in all three instances.

Walter J. Musliner, John W. Gates, Jr.
Kodak Research Laboratories
Eastman Kodak Company, Rochester, New York 14650
Received July 27, 1966

Cycloaddition Reactions of "Quadricyclanes"[1]

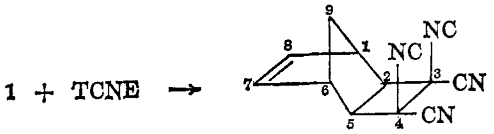
Sir:

We wish to report that quadricyclane (**1**) and certain of its derivatives cycloadd to ethylenic and acetylenic dienophiles giving 1:1 adducts with surprising stereospecificity. This may provide useful synthetic intermediates and stimulate further investigations of strained small-ring compounds.



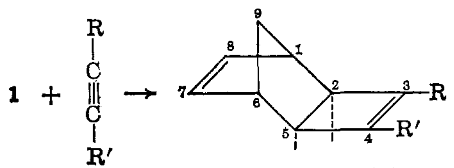
1

Specifically, **1** and tetracyanoethylene react exothermally in methylene chloride to give a crystalline 1:1 *exo* adduct, **2**,[2] isolated in 78% yield. Adduct **2** can be recrystallized from ethylene dichloride to give white needles melting at 166–167°. *Anal.* Calcd for $C_{13}H_8N_4$: C, 70.90; H, 3.66; N, 25.44. Found: C, 70.61; H, 3.72; N, 25.59.



2

The nuclear magnetic resonance spectrum (DMSO-d_6) showed two vinyl protons as a poorly resolved triplet at $\delta = 6.25$ ppm, two bridgehead protons as a broad singlet at $\delta = 3.30$ ppm, two protons as a singlet at $\delta = 3.00$ ppm, and two protons as a quartet at $\delta = 1.80$ ppm. We assigned the singlet at $\delta = 3.00$ ppm to the *endo* protons, C-2 and -5, and the quartet to the other two bridge protons, C-9 of **2**.



3, $R = R' = CO_2CH_3$
4, $R = R' = CN$
5, $R = H, R' = CO_2CH_3$

Negatively substituted acetylenes react rapidly with **1**; each gives a single 1:1 adduct (see Table I).

Table I. Adducts from Acetylenic Dienophiles and **1**

Compd	Mp or bp, °C (mm)	Mol wt Found	Mol wt Calcd	C, % Found	C, % Calcd	H, % Found	H, % Calcd	N, % Found	N, % Calcd	Yield, %
3	93–99(0.2)	235	234	66.45	66.66	5.88	6.02			74
4	133–134	168	168	78.63	78.55	4.77	4.79	16.38	16.66	78
5	52–53(0.2)	177	176	74.76	74.98	7.10	6.86			74

Table II. Spectral Data

		Ultraviolet				Near-infrared[a]			Infrared, cm⁻¹	
Compd	Solvent	λ_{max}, mμ	ϵ	λ_{max}, mμ	ϵ	Absorption peak μ	Absorption peak cm⁻¹	Molar absorptivity	$\nu_{C=O}$	$\nu_{C\equiv N}$
2						*b*				2248
3	EtOH	268	1910			1.660	6024	0.660	1730	
4	EtOH	283	1428	228	6440	1.655	5042	0.600		2220
5	EtOH	250	2410			1.660	6024	0.930	1728	
7	EtOH	264	2100	225[c]	5840	1.655	6042	0.730	1755 1735	

[a] Solutions were all CCl_4; see P. G. Gassman and W. M. Hooker, *J. Am. Chem. Soc.*, **87**, 1079 (1965). [b] Compound **2** was too insoluble for suitable near infrared spectrum. [c] Shoulder.

The structures of these adducts are supported by spectral data listed in Table II.

The stereochemistry of **2–5** is *exo* because the proton(s) at C-2 (C-5) do not couple with the proton(s) at C-1 (C-6). This is a well-documented[3] characteristic of norbornanes and norbornenes.

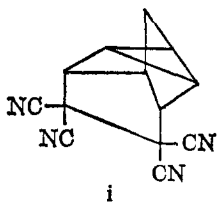
The remarkable steric preference of this cycloaddition was demonstrated when 7-acetoxyquadricyclane[4] (**6**) and dimethyl acetylenedicarboxylate gave >95%[5] *exo*-9-*anti*-acetoxytricyclo[4.2.1.0^{2,5}]nona-2,7-diene (**7**), mp 82–83. *Anal.* Calcd for $C_{15}H_{16}O_6$: C, 61.64; H, 5.52. Found: C, 61.75; H, 5.67.

1 and maleic anhydride formed a colored complex ($\lambda_{max}^{cyclohexane}$ 315 mμ (ϵ 1000)) which, after heating, gave

---

(1) For brevity, we use this name for tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (the IUPAC designation). Other widely used names are quadricyclo-[2.2.1.0^{2,6}.0^{3,5}]heptane and quadricyclene.

(2) Bicyclo[2.2.1]heptadiene reacts with tetracyanoethylene more slowly to give the tetracyclic isomer i: A. T. Blomquist and Y. C.



i

Meinwald, *J. Am. Chem. Soc.*, **81**, 667 (1959).

(3) (a) W. D. Kumler, J. N. Shoolery, and F. Brutcher, Jr., *ibid.*, **80**, 2533 (1958); (b) H. E. Simmons, *ibid.*, **83**, 1657 (1961); (c) E. I. Snyder and B. Franzus, *ibid.*, **86**, 1166 (1964); (d) P. Laszlo and P. von R. Schleyer, *ibid.*, **86**, 1171 (1964); (e) J. Meinwald, J. C. Meinwald, and T. N. Baker, III, *ibid.*, **86**, 4074 (1964).

(4) H. G. Richey, Jr., and N. C. Buckley, *ibid.*, **85**, 3057 (1963).

(5) Determined by the nmr spectrum of the crude reaction mixture. See ref 3c for nmr assignments of *syn*- and *anti*-substituted norbornenes and norbornadienes.