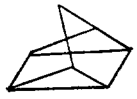
ethers[1] of the isomeric methoxy phenols gave anisole from *o*-, *m*-, and *p*-methoxyphenol in 60, 31, and 0% yields, respectively. The method described here for the 1-phenyl-5-tetrazolyl ethers gave anisole in over 80% yields in all three instances.

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]

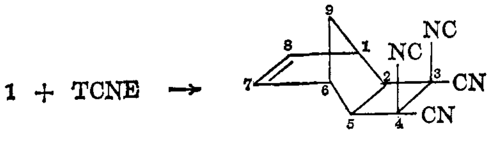
Sir:

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.



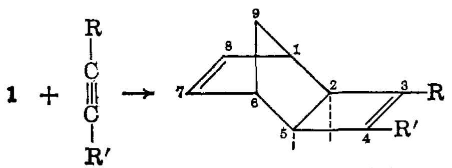
1

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

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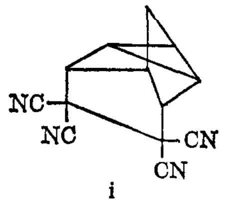
(1) For brevity, we use this name for tetracyclo[3.2.0.$0^{2,7}$.$0^{4,6}$]heptane (the IUPAC designation). Other widely used names are quadricyclo-[2.2.1.$0^{2,6}$.$0^{3,5}$]heptane and quadricyclene.

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



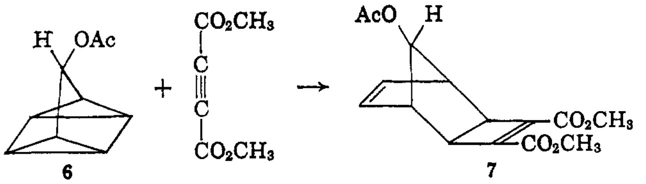
i

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).

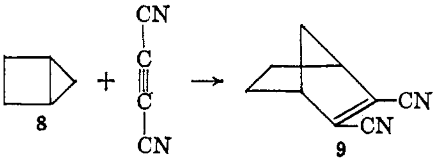
(5) Determined by the nmr spectrum of the crude reaction mixture. See ref 3c for nmr assignments of *syn*- and *anti*-substituted norbornenes and norbornadienes.



6 7

a 1:1 adduct. Adducts have been observed with a variety of other dienophiles and will be discussed in detail in a later paper.

We propose that this behavior of quadricyclane demonstrates a novel "diene-like" activity with a striking preference for *exo* attack by dienophiles. Gassman and Mansfield[6] have reported that bicyclo[2.1.0]pentane



8 9

(**8**) reacts slowly with dicyanoacetylene to give 2,3-dicyanobicyclo[2.2.1]hept-2-ene (**9**). This reaction is promoted in part by the strain energy built into the bicyclopentane system. A closely related reaction was reported recently by Cairncross and Blanchard[7] for bicyclobutanes.

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(6) P. G. Gassman and K. Mansfield, *Chem. Commun.*, 391 (1965).

(7) A. Cairncross and E. P. Blanchard, Jr., *J. Am. Chem. Soc.*, **88**, 496 (1966).

Claibourne D. Smith
Contribution No. 1222, Central Research Department
Experimental Station, E. I. du Pont de Nemours and Company
Wilmington, Delaware 19898

Received June 29, 1966

Direct Nucleophilic Substitution at the Central Carbon Atom of Triarylmethyl Substrates[1]

Sir:

The literature records no clear-cut example of nucleophilic substitutions on triarylmethyl substrates by the SN2 mechanism.[2] In this communication we report experimental results showing that if sufficiently deactivated substrates[3] and suitable conditions are used, the direct substitution mechanism may be made to compete effectively with, or even take over completely, the ionization mechanism.

Table I. First-Order Specific Rates of Isotopic Exchange between $(4\text{-}NO_2\text{–}C_6H_4)_3CCl$ and $Et_4N^{36}Cl$ in Acetone at 80° in the Presence of Et_4NClO_4

$Et_4N^{36}Cl$, $M \times 10^3$	0.945	1.91	4.91	9.92	0.957	1.91	4.89	9.91
Et_4NClO_4, $M \times 10^3$	8.99	7.96	4.98	. . .	98.9	98.0	95.0	90.0
Rate $\times 10^6$/[R–Cl], sec^{-1}	1.16	2.03	4.94	10.7	0.643	0.952	2.21	3.83

The results deal with the kinetics of isotopic exchange between ionic chloride (tetraethylammonium chloride-^{36}Cl) and 4,4′,4′′-trinitrotriphenylmethyl or 4,4′-dinitrotriphenylmethyl chloride in acetone. The experiments were carried out in the presence of a constant electrolyte concentration which was maintained at the preset value (0.01 or 0.1 *M*) by adding tetraethylammonium perchlorate. These working conditions effectively minimize the ambiguities which often arise in the borderline region of nucleophilic substitution.[5] The kind of experiment is illustrated in Table I which reports two series of runs for the tri-*p*-nitro substrate where the total electrolyte concentration was 0.01 (the first four entries) and 0.1 *M* (the last four entries), respectively.

The data of Table I as well as those similarly obtained for the same substrate in acetonitrile solvent, and for the di-*p*-nitro substrate in acetone, all fit satisfactorily the simple rate equation for concurrent first- and second-order processes: rate/[R–Cl] = $k_1 + k_2$[Et_4NCl]. Table II records the sets of k_1 and k_2, and their standard deviations, each obtained in 4–7 kinetic runs covering an approximately tenfold change of the nucleophile concentration.

Other significant observations are the following. (a) In the tri-*p*-nitro substrate (0.01 *M*) the rate of exchange is not affected by the presence of *m*-dinitrobenzene (up to 0.05 *M*). (b) Ionic azide (Bu_4NN_3) in acetone reacts with tri-*p*-nitrophenylmethyl chloride by a second-order process: at 80° the rate constant is 5.06×10^{-1} M^{-1} sec^{-1}, *i.e.*, about 500 times faster than the chloride exchange.

The first-order contribution to the rate appears to arise from a rate-determining ionization. Thus, while k_1 is nil within experimental error for the more deactivated substrate (tri-*p*-nitro) in the less polar medium (acetone, 0.01 *M* electrolyte), it becomes significantly greater than zero when the polarity of the medium is increased, either by increasing the electrolyte concentration to 0.1 *M* or by substituting acetone for acetonitrile, or when the substrate is made less deactivated (di-*p*-nitro). The experiments, however, tell nothing as to which particular ionization stage[6] may be involved.

The second-order term cannot arise from a positive salt effect on the first-order ionization process since the *over-all* exchange rate actually decreases with increasing salt concentration (Table I). Inspection of Table II shows the decrease is due to a diminishing importance of the second-order contribution with increasing salt.

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(1) Supported by Consiglio Nazionale delle Ricerche, Rome.

(2) For a discussion of nucleophilic substitution reactions on triarylmethyl systems see (a) A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 81; (b) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., Chapter VII.

(3) The need of having strong electron-attracting groups in the aryl moiety has recently been recognized by Patai and Zabicki[4] who used 4,4′,4′′-trinitrotriphenylmethyl chloride in a recent study of SN reactions.[4] However, their choice of acetic acid as the medium and the use of powerful electrophilic cations (lithium, silver, and mercury) in the nucleophilic salts were hardly suitable to fostering SN2-type reactions which in fact were not observed.[4]

(4) S. Patai and Zabicki, *J. Chem. Soc.*, 5479 (1961).

(5) (a) A. Fava, A. Iliceto, and A. Ceccon, *Tetrahedron Letters*, 685, (1963); (b) A. Ceccon, I. Papa, and A. Fava, *J. Am. Chem. Soc.*, in press.

(6) S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck, and C. G. Robinson, *ibid.*, **78**, 328 (1956).