mopropane, suggests a halogen atom shift similar to that implied by the present work, and Wiley[3] has referred to other examples. Clear-cut evidence for the abstraction of hydrogen from HCl by radicals has been observed in other work.[7]

This work was supported in part by the Atomic Energy Commission under contract AT(11-1)-32 and in part by the University Research Committee with funds made available by the Wisconsin Alumni Research Foundation.

(7) See, for example: (a) R. J. Cvetanovic and E. W. R. Steacie, *Canad. J. Chem.*, **31**, 158 (1953); (b) J. H. Raley, F. F. Rust and W. E. Vaughan, *J. Am. Chem. Soc.*, **70**, 2767 (1948).

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PHOTOSENSITIZED CYCLOADDITION REACTIONS[1]

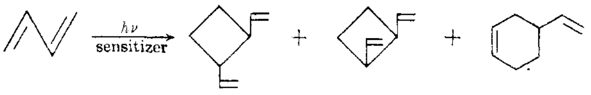
Sir:

We have recently reported[2] evidence for the production of triplet states of the conjugated dienes, *cis*- and *trans*-piperylene, by the following process of energy transfer

$$A_g \xrightarrow{h\nu} A_{S_1} \longrightarrow A_{T_1}$$

$$A_{T_1} + B_g \longrightarrow A_g + B_{T_1}$$

An obvious application of this procedure is the use of sensitizers to produce diene triplets which can, in turn, undergo chemical reactions. In order to demonstrate the principle we have carried out the dimerization of butadiene in the presence of several sensitizers. The reactions produce *cis*- and *trans*-1,2-divinylcyclobutane and 4-vinylcyclohexene in varying amounts.



In order to maximize yields, the reactions were run at −10° using neat butadiene plus the sensitizer. Quantum yields have not been measured but the rates are sufficiently high to allow recommendation of the reaction as a practical preparative procedure for *trans*-1,2-divinylcyclobutane. For example, 80 ml. of butadiene containing 15 ml. of 2,3-pentanedione was irradiated in a Hanovia Type S 200-watt quartz immersion apparatus for 80 hours. At the end of this time the mixture was analyzed by vapor chromatography. Only 4% unreacted butadiene remained and dimers were present in the ratios indicated in Table I. The products were isolated by preparative vapor chromatography. The physical constants and infrared spectra of the products agreed exactly with those reported in the literature.[3,4] *cis*-1,2-Divinylcyclobutane was further characterized by thermal conversion to 1,5-cyclooöctadiene.[4] The *trans*-isomer was oxidized with ozone to *trans*-1,2-cyclobutanedicarboxylic acid.[3] A 40-g. sample of the crude reaction mixture was worked up by conventional procedures. The diketone was removed by passage through an alumina column and the eluent then was heated under reflux at 120° for three hours to convert *cis*-1,2-divinylcyclobutane to 1,5-cyclooöctadiene. The mixture then was fractionated with a spinning band column; the fractions obtained were 15 g. of *trans*-1,2-divinylcyclobutane, b.p. 111–113°, n^{25}_{D} 1.4430; 12 g. of 4-vinylcyclohexene, b.p. 128°, n^{25}_{D} 1.4620; and 2 g. of 1,5-cyclooöctadiene, b.p. 150–155°, n^{25}_{D} 1.4930.

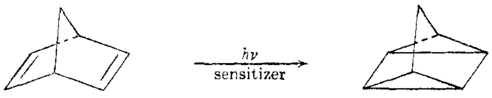
The data in Table I show that the composition of the mixture of dimers depends on the nature of the photosensitizer, a surprising result. The result is not a corollary of the theory of sensitized reactions in its present state. Various extensions of the theory can account for the results and further study of the phenomenon is in progress.

TABLE I

PRODUCTS FORMED IN PHOTODIMERIZATION OF BUTADIENE BY VARIOUS SENSITIZERS

Sensitizer	% *trans*-1,2-Divinylcyclobutane	% *cis*-1,2-Divinylcyclobutane	% 4-Vinylcyclohexene
Benzil	49	∼8	∼43
2,3-Pentanedione	44	12	42
Acetophenone	82	14	4
2-Acetonaphthone	76	17	7

Experiments designed to effect dimerization of mono-olefinic substances thus far have been only partially successful. If sensitizers having high energy triplets are used, isomerization of the 2-butenes can be observed and small yields of dimers have been produced in a number of instances. The problem is still under scrutiny and results will be reported later. However, we have found an interesting example of a facile internal addition. Irradiation of norbornadiene in isopentane solution with various sensitizers (acetone, acetophenone or benzophenone) led to rapid ring-closure with the formation of quadricyclene.[5]



The product was concentrated by fractional distillation (to quadricyclene: diene ratio of 18:1 as determined by v.p.c. analysis) and pure samples of quadricyclene were obtained by vapor chromatography, b.p. 108° (740 mm.), $n^{26.5}_{\mathrm{D}}$ 1.4830. The compound was characterized primarily by its n.m.r. spectrum and by virtue of the fact that it reverts to norbornadiene when heated to 140°. The n.m.r. spectrum of the diene shows the expected resonances due to the methylene group (184 c.p.s. relative to tetramethylsilane), the tertiary hydrogen atoms (−225 c.p.s.) and vinyl hydrogen (−410 c.p.s.). The latter two resonances are not present in the spectrum of the photoproduct which shows methylene resonance (−182 c.p.s.) and a broad group with the highest peak at −146 c.p.s. The latter group is assigned to the resonance of the six protons attached to the three-membered rings of quadricyclene. Integration indicates that the area under the broad group is 3.3 times the area of

(1) Mechanisms of Photoreactions in Solution. VII. Part VI is G. S. Hammond and P. A. Leermakers, *J. Am. Chem. Soc.*, in press.

(2) G. S. Hammond, P. A. Leermakers and N. J. Turro, *J. Am. Chem. Soc.*, **83**, 2396 (1961).

(3) H. W. B. Reed, *J. Chem. Soc.*, 685 (1951).

(4) E. Vogel, *Ann.*, **615**, 1 (1958).

(5) The same transformation has been carried out by direct irradiation; W. G. Dauben and R. L. Cargill, *Tetrahedron*, in press. We are indebted to Professor Dauben for prepublication disclosure of his results.

the methylene peak. Thermal reversion was observed by heating a degassed sample, originally containing 91% quadricyclene and 9% norbornadiene at 140° for 14 hours. At the end of that period the sample contained 56% quadricyclene and 44% diene. Vapor chromatography indicated the presence of no other products.

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RECEIVED SEPTEMBER 1, 1961

SODIUM ZEOLITE ZK-4, A NEW SYNTHETIC CRYSTALLINE ALUMINOSILICATE

Sir:

One of the most interesting and useful of the purely synthetic zeolites is zeolite A.[1] This is one of the few zeolites whose lattice composition has thus far been found to be essentially constant with an SiO_2/AlO_2 molar ratio of 0.96 ± 0.05.[1,2] This apparent constancy of composition has been a matter of curiosity to some structural chemists interested in zeolites.

We recently synthesized a zeolite whose crystal structure is similar to, but whose chemical composition differs significantly from, zeolite A. Like zeolite A, the new compound (designated zeolite ZK-4) contains 24 tetrahedra in a cubic unit cell. The unit cell formula of sodium zeolite ZK-4 is $Na_9[(AlO_2)_9(SiO_2)_{15}]\cdot 27H_2O$ compared with $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]\cdot 27H_2O$ for sodium zeolite A. Because of the high SiO_2/AlO_2 ratio of zeolite ZK-4, a contraction of the unit cell compared with sodium zeolite A (a_0 = 12.32 Å.) is expected since the Si–O bond distance is shorter than the Al–O bond distance. X-Ray diffraction analysis disclosed a_0 = 12.16 ± 0.02 Å. for sodium zeolite ZK-4. By the method of Smith,[3] the unit cell of the new zeolite subsequently was calculated to be 1.33% smaller than that of sodium zeolite A or a_0 = 12.15 Å. A summary of pertinent X-ray diffraction data for sodium zeolite ZK-4 is presented in Table I.

Some of the molecular sieve properties of sodium zeolite ZK-4 are markedly different from those of sodium zeolite A as shown in Table II.

TABLE I

X-RAY DIFFRACTION DATA—SODIUM ZEOLITE ZK-4

(h,k,l)	d, Å.	I/I_{max}	(h,k,l)	d, Å.	I/I_{max}
100	12.07	100	600	2.033	4
110	8.57	71	621	1.904	2
111	7.025	50	541	1.881	1
210	5.422	23	622	1.835	1
220	4.275	11	630	1.813	1
300	4.062	48	444	1.751	1
311	3.662	59	632	1.737	1
320	3.390	33	710	1.718	4
321	3.244	64	641	1.669	4
410	2.950	60	721	1.653	1
411	2.862	14	722	1.611	1
420	2.727	8	730	1.595	1
421	2.661	4	650	1.558	1
332	2.593	13	652	1.510	1
422	2.481	2	811	1.501	1
430	2.435	1	821	1.465	1
511	2.341	2	653	1.450	1
521	2.225	2	831	1.415	1
440	2.162	2	751	1.405	1
441	2.120	1	654	1.385	1
530	2.080	1	744	1.349	1
531	2.061	1	910	1.345	1

TABLE II

ADSORPTIVE CAPACITIES OF ZEOLITES ZK-4 AND A AT ROOM TEMPERATURE

	G. sorbed/100 g. activated zeolite[a]			
	n-Hexane	n-Octane	3-Methylpentane	Water
NaA	0.4(20)	0.5(13)[1c]	0.3(20)	28.9(24)[1b]
CaA	12.6(20)	15.4(11)[1c]	.2(20)	30.5(24)[1b]
KA	0.2(20)	0 (11)[1c]	.2(20)	22.2(19)[1c]
NaZK-4	12.5(20)	12.6(11)	.2(20)	24.8(12)
KZK-4	0.4(20)	0.3(11)	.2(20)	19.5(12)

[a] Vapor pressure, mm., of adsorbate in equilibrium with adsorbent given in parentheses.

Of particular significance is the ability of sodium zeolite ZK-4 to adsorb appreciable quantities of *n*-paraffins compared with sodium zeolite A. This property of the new zeolite probably is related to the smaller number of sodium ions per unit cell compared with sodium zeolite A. When 30 to 40% of the sodium ions in zeolite A are replaced by calcium ions, the resulting zeolite is capable of adsorbing straight chain hydrocarbons. At this level of exchange the unit cell of zeolite A contains an average of 9.6 to 10.2 cations. These data suggest that perhaps the nine sodium ions in zeolite ZK-4 occupy sites in the lattice similar to those occupied by the cations in calcium exchanged sodium zeolite A. Studies are currently underway in an attempt to establish the location of monovalent cations in the new zeolite. As shown in Table II, the new sodium zeolite can separate straight-chain from branched-chain hydrocarbons and potassium zeolite ZK-4 can separate water from both straight-chain and branched-chain hydrocarbons.

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[1] (a) D. W. Breck, W. G. Eversole and R. M. Milton, *J. Am. Chem. Soc.*, **78**, 2338 (1956); (b) D. W. Breck, W. G. Eversole, R. M. Milton, T. B. Reed and T. L. Thomas, *ibid.*, **78**, 5963 (1956); (c) R. M. Milton, U. S. Patent 2,882,243 (1959).

[2] R. M. Barrer and W. M. Meier, *Trans. Faraday Soc.*, **54**, 1074 (1958).

[3] J. V. Smith, *Acta Cryst.*, **7**, 479 (1954).

REACTIONS OF THE *t*-NITROBUTYL ANION RADICAL

Sir:

Although the e.s.r. spectra of anion radicals of aromatic nitro and dinitro compounds have been studied,[1,2,3,4] no similar information is available for aliphatic nitro compounds. In contrast to the stable anion radicals derived from either sub-

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[1] R. L. Ward, *J. Chem. Phys.*, **30**, 852 (1959).

[2] D. H. Geske and A. H. Maki, *J. Am. Chem. Soc.*, **82**, 2671 (1960).

[3] R. L. Ward, *ibid.*, **83**, 1296 (1961).

[4] A. H. Maki and D. H. Geske, *J. Chem. Phys.*, **33**, 825 (1960).