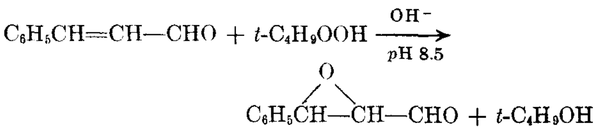
major product appeared to be an organic peroxide rather than the desired epoxy aldehyde, the reaction was carried out with *tert*-butyl hydroperoxide as oxidant rather than hydrogen peroxide.


I

Cinnamaldehyde and *tert*-butyl hydroperoxide were allowed to react in *methanol* solution at 35–40° for five to six hours while dilute sodium hydroxide was added continuously to neutralize acidic by-product and maintain a *p*H of about 8.5. β-Phenylglycidaldehyde (I) was readily obtained in 73% yield by Claisen-distillation of the crude product.

While this epoxidation of cinnamaldehyde by means of alkaline *tert*-butyl hydroperoxide appears to be the first such reaction with an α,β-unsaturated aldehyde, the corresponding reaction with α,β-unsaturated ketones has recently been described.[2] In that work, *benzene* was the solvent and no attempt was made to operate with controlled *p*H. When such a procedure was used with cinnamaldehyde, the crude product was mainly an organic peroxide (possibly *via* Michael addition); it was not further investigated.

EXPERIMENTAL

Epoxidation of cinnamaldehyde. To a 1-l., 5-neck, round bottom flask equipped with mechanical stirrer, dropping funnels, thermometer, and standard electrodes connected to a Beckman *p*H meter, were added 400 ml. of methanol and 71.2 g. (0.60 mol.) of *tert*-butyl hydroperoxide (Lucidol, 75.9% by iodometric titration). The meter *p*H was adjusted to 10.5 ± 0.2 (true *p*H of about 8.5 by indicator paper) by the addition of *N* sodium hydroxide and maintained there as 66 g. (0.50 mol.) of freshly distilled cinnamaldehyde was added at 35–40° over 1 hr. After another 4.5 hr., iodometric titration indicated that 0.48 mol. of hydroperoxide had been consumed and the reaction had essentially stopped; 20 ml. of alkali (4 mol. %) was utilized in maintaining the desired *p*H.

After dilution with 1.5 l. of water and extraction by three 200-ml. portions of chloroform, the combined extracts were washed, dried, concentrated to low volume under vacuum and finally Claisen-distilled. There was thus obtained 54 g. (73% yield) of β-phenylglycidaldehyde, b.p. 66–68° (0.2 mm.), n_D^{20} 1.5447. The infrared spectrum showed aldehyde carbonyl absorption at 5.76 μ and epoxide absorption at 8.14 and 11.50 μ.

Anal. Calcd. for $C_9H_8O_2$: C, 73.0; H, 5.4; carbonyl value, 0.68 equiv./100 g.; oxirane oxygen, 10.8. Found: C, 72.9; H, 5.7; carbonyl value, 0.69 equiv./100 g.; oxirane oxygen, 6.7.[3]

The *2,4-dinitrophenylhydrazone* was prepared from 3.0 g. of epoxy aldehyde by adding the latter to a hot solution of 4.0 g. of 2,4-dinitrophenylhydrazine and 2 ml. of acetic acid in 300 ml. of ethanol. After boiling for 1 min., the solution was cooled quickly to 60° and filtered. After standing overnight at room temperature, the derivative was recovered by filtration and washed well with ethanol. The weight of material melting at 138–139° was 3.3 g.

Anal. Calcd. for $C_{15}H_{12}N_4O_5$: N, 17.0. Found: N, 16.9.

Shell Development Co.
Emeryville, California

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(2) N. C. Yang and R. A. Finnegan, *J. Am. Chem. Soc.*, **80**, 5845 (1958).

(3) Hydrochloric acid in dioxane; see J. L. Jungnickel, E. D. Peters, A. Polgar, and F. T. Weiss, "Organic Analysis, Vol. 1," Interscience Publishers, Inc., New York, 1953, p. 135; *in a blank experiment, styrene oxide itself gave an oxirane oxygen value of only 88% of theory.*

Diels-Alder Diene Synthesis With 1,1,1-Trichloro-3-nitropropene[1]

Howard Burkett and William Wright

Received August 20, 1959

Although many examples of the Diels-Alder reaction for aromatic substituted nitroolefins, such as β-nitrostyrene and substituted β-nitrostyrenes, have been published,[2] few have been reported for non-aromatic nitroolefins. Nitroethene,[3,4] 1-nitro-1-propene,[3] 1-nitro-1-pentene,[3] 1-nitro-1-heptene,[5] 1-nitro-1-octene,[5] 2-nitropropene,[6,7] 2-nitro-1-butene[6] and 2-nitro-2-butene[7] react with cyclopentadiene to yield the normal Diels-Alder adduct in 33 to 72% yield. Both aromatic and non-aromatic nitroolefins react with anthracene[8] in yields up to 62%. Substituents on the nitroolefins reduce the yield[8] or appear to cause the reaction to proceed with greater difficulty.[5]

The present study was undertaken to learn the effect of the sterically bulky, electron attracting trichloromethyl group in 1,1,1-trichloro-3-nitropropene[9] (I) upon the Diels-Alder reaction. The dienes used were butadiene-1,3 (IIa), isoprene (IIb), pentadiene-1,3 (IIc), 2,3-dimethylbutadiene-1,3 (IId), cyclopentadiene (IIe), 2-chlorobutadiene-1,3,furan and 2,5-dimethylfuran. The latter two compounds were chosen because they react with less facility or fail to react in the Diels-Alder re-

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(1) Supported in part by a grant from Research Corporation to whom the authors are grateful. Taken in part from the Masters thesis of W. W.

(2) For example: W. C. Wildman, R. B. Wildman, W. T. Norton, and J. B. Fine, *J. Am. Chem. Soc.*, **75**, 1912 (1953).

(3) K. Alder, H. Rickert, and E. Windemuth, *Ber.*, **71**, 2451 (1938).

(4) W. C. Wildman and C. H. Hemminger, *J. Org. Chem.*, **17**, 1641 (1952); J. D. Roberts, C. C. Lee and W. H. Saunders, Jr., *J. Am. Chem. Soc.*, **76**, 4501 (1954).

(5) W. E. Noland, R. E. Counsell, and M. H. Fisher, *J. Org. Chem.*, **21**, 911 (1956).

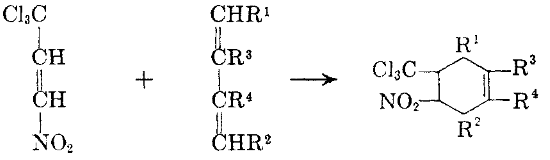
(6) D. V. Nightingale, M. Maienthal, and J. A. Gallagher, *J. Am. Chem. Soc.*, **75**, 4852 (1953).

(7) W. E. Noland and R. E. Bambury, *J. Am. Chem. Soc.*, **77**, 6386 (1955).

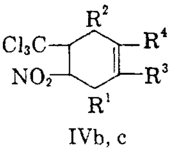
(8) W. E. Noland, H. I. Freeman, and M. S. Baker, *J. Am. Chem. Soc.*, **78**, 188 (1956).

(9) F. Brower and H. Burkett, *J. Am. Chem. Soc.*, **75**, 1082 (1953).

action. For example, both are reported not to react with β-nitrostyrene.[10]


I IIa, b, c, d, e IIIa, b, c, d, e

	R^1	R^2	R^3	R^4
II and III a.	H	H	H	H
b.	H	H	CH_3	H
c.	CH_3	H	H	H
d.	H	H	CH_3	CH_3
e.	—CH_2—		H	H


IVb, c

The dienes listed, except the two furans and 2-chlorobutadiene-1,3, reacted with I to yield adducts in 65 to 88% yield. Attempts with the furans included standing at room temperature for thirty days without solvent, refluxing without solvent and refluxing in acetic acid. In each case both the furan and I were recovered and there was no residue. In all of the attempts with the 2-chlorobutadiene, I was completely or nearly completely recovered. The remainder of the reaction mixture was a non-distillable, resinous material. This reaction was tried, without solvent, in xylene and in acetic acid; with temperatures between room temperature and that of refluxing xylene; and with reaction times from four hours to nineteen days. In most of the attempts hydroquinone was added to inhibit polymerization.

Although no experiments were performed to prove the position of the double bond in the products, the infrared spectrum for each product was consistent with that expected for the normal Diels-Alder product.[11]

Two position isomers are possible for the products from both IIb and IIc. Treatment of the adduct from IIb with palladium on charcoal produced 4-methyl-2-nitrobenzoic acid. Heating the same material with concentrated sulfuric acid produced *m*-toluic acid. Evidently, the product contained both isomers, IIIb and IVb. No attempt was made to separate them. Although the presence of isomeric compounds in the product from IIc was not investigated, it probably contained both IIIc and IVc.

Whereas the reaction with IIe was exothermic and essentially complete at 35–50° within a few hours, that using IIa was quite slow. Table I indicates the percent yield isolated from reactions carried out at room temperature for different lengths of time. Maximum yields were obtained only when the reaction time was over two weeks. As the reaction was not exothermic for any of the other compounds, each was allowed to react at room temperature for at least two weeks before distilling.

TABLE I

PERCENT YIELD VS. REACTION TIME FOR BUTADIENE

Time (days)	Yield, %
0.25	1.7
0.5	3.5
1	7.8
3	19.5
6	37
8	50
11	65
15	78

EXPERIMENTAL

Dienes. 2-Chlorobutadiene-1,3 was distilled from a chloroprene-xylene mixture obtained from E. I. du Pont de Nemours.[12] The 1,3-butadiene (special purity grade), isoprene (polymerization grade), and pentadiene-1,3 were supplied by the Phillips Petroleum Company.[12] The 2,3-dimethylbutadiene-1,3 was supplied by the Borden Company.[12] Cyclopentadiene was obtained by the thermal depolymerization of dicyclopentadiene from the Enjay Company.[12]

2-Nitro-1,2,3,6-tetrahydrobenzotrichloride (IIIa). For each run 32.5 g. (0.6 mol.) of 1,3-butadiene and 80 g. (0.45 mol.) of I were sealed in a heavy-walled bottle. After the length of time given in Table I each mixture was distilled under reduced pressure. The yield of product was taken to be that distilling at *ca.* 109–112°/1 mm. The crude product from a run allowed to stand for 18 days was carefully fractionated, yielding 71 g. (67%) of a very pale yellow oil, b.p. 110–111°/1 mm., d^{20}_{20} 1.4801, n^{20}_{D} 1.5317.

Anal. Calcd. for $C_7H_8Cl_3NO_2$: N, 5.73; Cl, 43.52. Found: N, 5.74; Cl, 43.70.

4-Methyl-2-nitro-1,2,3,6-tetrahydrobenzotrichloride (IIIb) *and 5-methyl-2-nitro-1,2,3,6-tetrahydrobenzotrichloride* (IVb). A solution of 15 g. (0.22 mol.) of isoprene (IIb) and 39 g. (0.22 mol.) of I was placed in a stoppered flask. After 25 days the mixture was fractionated, yielding 48 g. (84.5%) of pale yellow oil, b.p. 117–118°/1 mm., d^{20}_{20} 1.4119, n^{20}_{D} 1.5271.

Anal. Calcd. for $C_8H_{10}Cl_3NO_2$: N, 5.42; Cl, 41.14. Found: N, 5.49; Cl, 41.23.

Evidence for IIIb in the product from isoprene. A mixture of 20 g. of the product from isoprene and 5 g. of 10% palladium on charcoal was heated in a flask at 190° until no more gas was evolved. The cooled residue was pulverized and extracted with three 40-ml. portions of ether. Evaporation of the ether left a brown sticky residue. Distillation gave 2.0 g. of a liquid, which solidified. Sublimation afforded a pale yellow product, m.p. 161–163°. The reported[13] melting point for 4-methyl-2-nitrobenzoic acid is 161°. The product was converted,[14] via the acid chloride, m.p. 158–160°, to the amide, m.p. 150–152°. The reported[13] melting points are 157° and 153°, respectively.

Evidence for IVb in the product from isoprene. The product (14 g.) was dissolved with cooling in 50 ml. of concentrated sulfuric acid. After standing at room temperature for 4 hr. and heating on the steam bath for 5 hr., the mixture was cooled and poured onto 125 g. of ice. After filtering, the

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[10] C. F. H. Allen and A. Bell, *J. Am. Chem. Soc.*, **61**, 521 (1939).

[11] The authors are indebted to Dr. Harold Boaz of Eli Lilly and Company for help in interpreting the spectra.

[12] The authors are grateful to these companies for complementary samples.

[13] C. Joachim, *Ann.*, **266**, 210 (1891).

[14] S. M. McElvain, "The Characterization of Organic Compounds," The MacMillan Company, New York, N. Y., 1945, p. 193.

resulting solid was extracted with 225 ml. of boiling water in six portions. Chilling in ice and filtering left a brown crystalline solid. This was extracted with boiling 90–100° ligroin, decanting from the insoluble dark oil. Cooling and filtering yielded 0.8 g. of white crystals, m.p. 110.5–111.5°. The reported melting point for *m*-toluic acid is 111–112°. This product was converted,[14] *via* the acid chloride, to the amide, m.p. 93–94° (lit.[14] 94°).

3-Methyl-2-nitro-1,2,3,6-tetrahydrobenzotrichloride (IIIc) *and/or 6-methyl-2-nitro-1,2,3,6-tetrahydrobenzotrichloride* (IVc). A mixture of 15 g. (0.22 mol.) of pentadiene-1,3 and 39 g. (0.22 mol.) of I was allowed to stand in a stoppered flask for 14 days. Fractionation afforded 26 g. (65%) of pale yellow liquid, b.p. 110–111.5°/1 mm., d_{20}^{20} 1.3626, n_D^{20} 1.5232.

Anal. Calcd. for $C_8H_{10}Cl_3NO_2$: N, 5.42; Cl, 41.14. Found: N, 5.32; Cl, 41.34.

4,5-Dimethyl-2-nitro-1,2,3,6-tetrahydrobenzotrichloride (IIId). A mixture of 18 g. (0.22 mol.) of 2,3-dimethylbutadiene-1,3 and 39 g. (0.22 mol.) of I was allowed to stand in a stoppered flask at room temperature for 14 days. Fractionation gave 41 g. (69%) of pale yellow liquid, b.p. 118–119°/1 mm., d_{20}^{20} 1.4225, n_D^{20} 1.5253.

Anal. Calcd. for $C_9H_{12}Cl_3NO_2$: N, 5.14; Cl, 39.05. Found: N, 5.17; Cl, 39.21.

3,6-Endomethylene-2-nitro-1,2,3,6-tetrahydrobenzotrichloride (IIIe). To 78 g. (0.44 mol.) of cold I was added 31 g. (0.44 mol.) of cold freshly-prepared cyclopentadiene in 3-ml. portions with swirling and cooling in an ice bath so that the temperature was maintained at 35–50°. When the mixture was no longer exothermic, the container was stoppered and allowed to stand at room temperature. Fractionation yielded 98 g. (87.5%) of pale yellow liquid, b.p. 113.5–115°/1 mm., d_{20}^{20} 1.4831, n_D^{20} 1.5334.

Anal. Calcd. for $C_8H_8Cl_3NO_2$: N, 5.50; Cl, 41.45. Found: N, 5.40; Cl, 41.04.

Department of Chemistry
DePauw University
Greencastle, Indiana

Reactions of Allene. I. Diels-Alder Adducts

H. Pledger, Jr.

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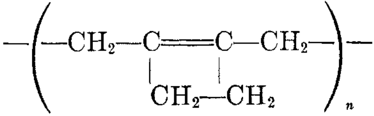
The Diels-Alder reaction between simple olefins and dienes is known[1] The same reaction between dienes and activated double bonds has received much attention.[2] However, the Diels-Alder reaction between dienes and compounds possessing cumulated double bonds has received very limited study.[3]

In this laboratory the Diels-Alder reactions between allene, which contains cumulated double bonds, and several conjugated dienes were studied. These Diels-Alder adducts were sought as intermediates for other studies now in progress in this laboratory. We wish to report at this time some results on cyclopentadiene and hexachlorocyclopentadiene.

Cyclopentadiene reacted with allene yielding four isolable products (II and III were not previously known): 5-methylenebicyclo[2.2.1]-2-heptene (I);[4] 1,2,3,4,4a,5,8,8a-octahydro-2-methylene-1,4,5,8 - dimethanonaphthalene (II); 1,2,3,4,4a,5,5a,6,9,9a,10,10a-dodecahydro-2-methylene-1,4,5,10,6,9-trimethanoanthracene (III); and a polymer (IV). The structures of the cuts corresponding to compounds II and III have not been proved but are probably as named. The characterization of IV has not been made, but collected data does not refute Lebedev and Merezhkovskii's[5] presumption that the polymerization of allene in metallic vessels yields a polymer of the structure  $-\left(-CH_2-\underset{|}{C}=\underset{|}{C}-CH_2-\right)_n-$ with CH_2-CH_2 bridging the two C atoms. Average molecular weight coupled with percent unsaturation would indicate that the average value of *n* is 11.5 in the particular sample of polymer reported here. Three different elemental analyses gave total carbon and hydrogen of about 95–97%. Mass spectroscopy analyses showed water present in the polymer. The infrared absorption at 11.45 μ is indicative of terminal unsaturation at the polymer chain end. While higher adducts such as four or five diene molecules to one of allene may have been formed in this reaction, they were in such low concentration that they were not isolated by distillation of the reaction mixture.

Hexachlorocyclopentadiene (V) reacted with allene yielding only one isolable product which was previously unknown: 1,2,3,4,7,7-hexachloro-5-methylenebicyclo [2.2.1]-2-heptene (VI). As would be expected, V reacted with allene at a lower temperature than cyclopentadiene and the yield of VI was higher than for I. No higher molecular weight adducts or polymer was isolated or indicated.

EXPERIMENTAL[6]

Allene. Fractional distillation of Dow methylacetylene–propadiene mixture (30% allene and 70% methylacetylene) at atmospheric pressure through a 60-inch glass, helices packed column yielded allene, b.p. −34.8° to −33.9°, having 98+% purity which was stored in steel cylinders until used.

Cyclopentadiene was prepared as 99+% pure material, b.p. 41–43°, by pyrolysis of Enjay dicyclopentadiene. The

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(1) L. M. Joshel and L. W. Butz, *J. Am. Chem. Soc.*, **63**, 3350 (1941).

(2) H. L. Holmes, "Organic Reactions," John Wiley and Sons, Inc., New York, 1948, Vol. IV, 60.

(3) von O. Diels and W. Friedrichsen, *Ann.*, **513**, 145 (1934); O. Wickterle and J. Rocek, *Chem. Listy*, **47**, 1768 (1953); *Coll. Czechoslov. Chem. Comm.*, **19**, 282 (1954).

(4) This compound was made by dehydrobromination of the Diels-Alder adduct between allyl bromide and cyclopentadiene and was presented by P. von R. Schleyer and R. E. O'Connor before the Division Organic Chemistry, American Chemical Society, Chicago, Ill., September, 1958, Paper No. 66.

(5) S. V. Lebedev and B. K. Merezhkovskii, *J. Russ. Phys. Chem. Soc.*, **45**, 1249.

(6) Boiling points are uncorrected. Elemental analyses were carried out by Galbraith Laboratory, Knoxville, Tennessee. Yields are calculated on charged reactant as noted.