isomers (*cf.* Table I) is in essential agreement with that obtained during preparation of the Grignard reagent. Thus, whatever mechanism is involved in the reaction of butenylmagnesium bromide with butenyl bromide, the factors controlling isomer distribution give results quite similar to those resulting from coupling of the butenyl radical.

EXPERIMENTAL[10]

Butenyl Grignard reagent was prepared according to the procedure of Young, Prater, and Winstein[8] from 1.5 moles of magnesium turnings and 0.5 mole of crotyl bromide.[11] There was used a total of 1 l. of anhydrous ether, and the bromide was added during about 4 hr.

Titration[12] of the solution of Grignard reagent indicated yields, in several runs, between 70 and 80%. In one run, the solution of Grignard reagent was concentrated by distillation of about 75% of the ether. Within the limits of experimental error (±10%), the assay by titration remained unchanged.

In a run in which the Grignard reagent was decomposed with water soon after it had been prepared, there was a violent reaction and evolution of large quantities of gas (not trapped). Work-up of the ether solution and distillation yielded 8.1 g. (25%) of a mixture of octadienes, b.p. 99–124°. This mixture was subjected to analysis by gas chromatography, with the results reported in Table I; no crotyl bromide was present. The infrared spectrum of the octadiene mixture exhibited absorption bands at the following wave lengths (μ): 3.32, 3.41 (doublet), 6.05, 6.82, 7.00, 7.25, 10.04, 10.32, 10.95.

Reaction of the butenyl Grignard reagent with cadmium chloride. A solution of Grignard reagent prepared as described above was transferred under nitrogen pressure to another flask in order to remove the large excess of magnesium. Assay of the transferred solution by titration was the same within experimental error (±3%) as before transfer. After there had been added over a 3-min. period 0.43 mole of anhydrous cadmium chloride, the mixture was stirred and heated under reflux until the Gilman test for Grignard reagent had become negative.[13] Titration[12] of the mixture after this period showed the presence of no material-consuming acid.

To the mixture was added 100 ml. of water, then the ether layer was separated, washed with water, and dried with magnesium sulfate. The bulk of the ether was removed by fractional distillation and the residue was subjected to analysis by gas chromatography (*cf.* Table I). Distillation[10] yielded a total of 21.7 g. (78%) of octadienes, b.p. 99–124°. This material was distributed in three main fractions: (1) b.p. 99–109°, n_D^{25} 1.4154–1.4209; (2) b.p. 110–114°, n_D^{25} 1.4233–1.4259; (3) b.p. 118–124°, n_D^{25} 1.4302–1.4309. For the isomeric octadienes (*cf.* formulas in text) there have been reported:[9] (III) b.p. 102°, n_D^{20} 1.4211; (IV) b.p. 111°, n_D^{20} 1.4240; (V) b.p. 124°, n_D^{20} 1.4336. Gas chromatography of the three fractions showed incomplete separation, as would be judged from the boiling point range; however, bands for only three components were observed, and the major band in each fraction was that expected from a correlation of retention time with boiling point.

The infrared spectrum of this mixture of octadienes was nearly identical with that exhibited by the mixture obtained directly from the preparation of Grignard reagent.

In one run, before cadmium chloride was added, a gas absorption line was arranged so that any exit gases would pass through two tubes of bromine thermostatted at 30° and then through a trap cooled in Dry Ice. Periodically, the flask and train were flushed with nitrogen. After the negative test for Grignard reagent had been obtained, the bromine was decomposed with sodium bisulfite; no water insoluble material was obtained. Also, no liquid was retained by the cold trap. A new absorbing train was put in place before water was added to the mixture. Again, no volatile gases were recovered.

In the run in which reaction with cadmium chloride was accelerated by concentration of the ether solution, results were essentially the same as when the dilute solution was utilized. Analysis of the octadiene mixture is included in Table I.

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(10) Boiling points are uncorrected; distillations were through a 65 cm. column of the simple Podbielniak design (*cf.* J. Cason and H. Rapoport, *Laboratory Text in Organic Chemistry*, Prentice-Hall, Inc., Englewood Cliffs, 1950, p. 237). Infrared spectra were recorded on a Baird spectrophotometer, using thin films.

(11) Gas chromatography of the "crotyl" bromide on silicone grease as partitioning agent indicated a composition of 11% methylallyl bromide and 89% crotyl bromide. Since the Grignard reagents from these two bromides have been found to be indistinguishable [*cf.* R. H. DeWolfe and W. G. Young, *Chem. Revs.*, **56**, 735 (1956)], it was deemed not worthwhile to separate the minor content of methylallyl bromide.

(12) H. Gilman, P. D. Wilkinson, W. P. Fishel, and C. H. Meyers, *J. Am. Chem. Soc.*, **45**, 150 (1923).

(13) The cadmium reagent gives a negative result in this test [*cf.* H. Gilman and J. F. Nelson, *Rec. trav. chim.*, **55**, 518 (1936)]. In the dilute solution in which the Grignard reagent was prepared, about 12 hr. elapsed before the test was negative, but in a run in which the solution was concentrated to one-fourth volume the test became negative after about 30 min. under reflux. The slow reaction with cadmium chloride in dilute ether solution has been noted on several previous occasions in this laboratory.

Preparation and Spectra of Some Dinitroparaffins

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The only method reported in the literature for preparing α,ω-dinitroparaffins has been the classical Victor Meyer reaction in which the appropriate diiodoalkane was treated with silver nitrite in an ethereal solution.[2] A recent study has demonstrated, however, that this reaction is really useful only for the synthesis of primary nitroparaffins.[3] This note describes the preparation and spectra of a series of α,ω-dinitroparaffins and a comparable secondary dinitro compound.

The α,ω-dinitroparaffins can be successfully prepared by treating the appropriate dibromoalkane with sodium nitrite in *N,N*-dimethylformamide:

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(1) This investigation was supported in part by a Research Grant from Socony Mobil Oil Company, Inc., Paulsboro, New Jersey.

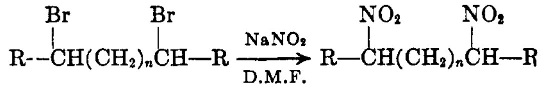
(2) H. Feuer and G. Leston, *Org. Syntheses*, **34**, 37 (1954).

(3) N. Kornblum, B. Taub, and H. Ungnade, *J. Am. Chem. Soc.*, **76**, 3209 (1954); N. Kornblum, R. Smiley, H. Ungnade, A. White, and S. Herbert, *J. Am. Chem. Soc.*, **77**, 5528 (1955).

TABLE I

Dinitro- paraffin	Yield,[a] %	M.P.	B.P.	n_D^{20}	Infrared (NO$_2$)	Cm.$^{-1}$
1,6-Dinitrohexane	42	36–37°[b]	100–103°/0.3 mm.		1550	1385
1,5-Dinitropentane	29		113–115°/0.2 mm.[c]	1.4597[c]	1550	1383
1,4-Dinitrobutane	33	33.5–34.5°[d]			1550	1379
1,3-Dinitropropane	6		100–101°/0.5 mm.[e]	1.4635[e] (25°)	1550	1385
2,5-Dinitrohexane[f]	7	51–52°			1538	1389 1357 1317

[a] Pure compound. [b] Lit.[2] m.p. 36.5–37.5°. [c] Lit.[3] b.p. 134°/1.2 mm., n_D^{20} 1.4610. [d] Lit.[3] m.p. 33–34°. [e] Lit.[12] b.p. 103°/1.0 mm., n_D^{25} 1.4638. [f] *Anal.* Calcd. for $C_6H_{12}N_2O_4$: C, 40.90; H, 6.87; N, 15.90. Found: C, 41.02; H, 6.96; N, 15.61.



$$\mathrm{R{-}\overset{Br}{\overset{|}{C}}H(CH_2)_n\overset{Br}{\overset{|}{C}}H{-}R \xrightarrow[D.M.F.]{NaNO_2} R{-}\overset{NO_2}{\overset{|}{C}}H(CH_2)_n\overset{NO_2}{\overset{|}{C}}H{-}R}$$

$R = H, CH_3 \quad n = 1 - 4$

The yields of pure products decrease with decreasing size of the alkyl portion of the molecule and a low yield is observed in the preparation of the secondary dinitroparaffin, 2,5-dinitrohexane. Apparently steric hindrance plays an important role in this reaction and thus reduces the applicability of the procedure for the lower members of the series.[4] (Table I). The preparation of 1,6-diiodo-1,6-dinitrohexane is also described.

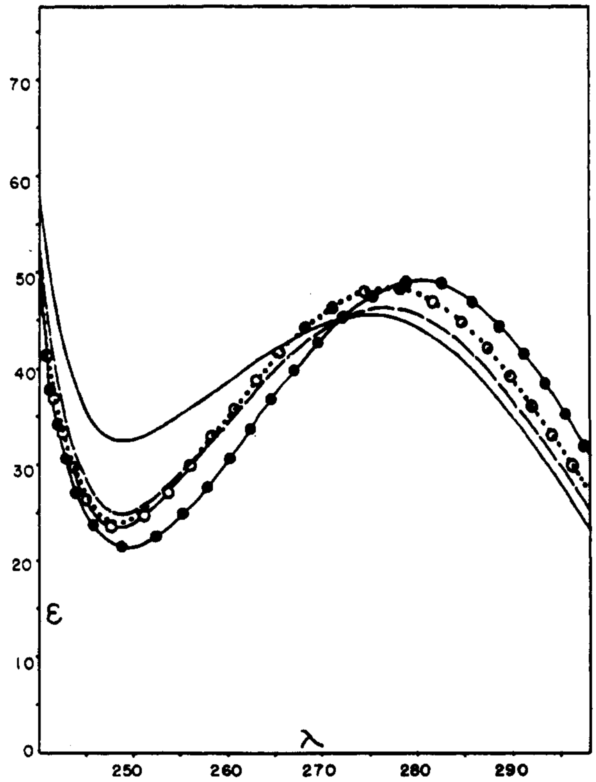


Fig. 1. Ultraviolet spectra of dinitroparaffins in 95% ethanol

—— 1,3-Dinitropropane —○— 1,6-Dinitrohexane
— — 1,4-Dinitrobutane —●— 2,5-Dinitrohexane
..... 1,5-Dinitropentane

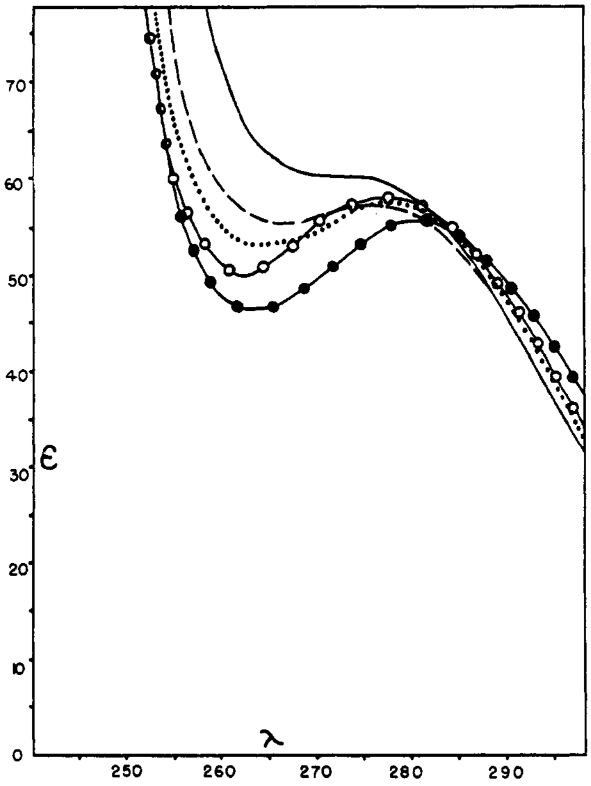


Fig. 2. Ultraviolet spectra of dinitroparaffins in dioxane

—— 1,3-Dinitropropane —○— 1,6-Dinitrohexane
— — 1,4-Dinitrobutane —●— 2,5-Dinitrohexane
..... 1,5-Dinitropentane

Aliphatic nitroparaffins are characterized by a low intensity, broad absorption band in the ultraviolet region at 270–280 mμ and a second high intensity band which lies below 200 mμ.[5,6] No fine structure is observed in the 280 mμ band. Solvent effects on the ultraviolet spectra of nitroparaffins and for nitromethane.[6,7] In those studies benzene, toluene, and dioxane were "active" solvents and increased the intensity of absorption as compared with a series of nonactive solvents. This perturbation has been considered to arise

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(4) D. Mooberry, Ph.D. Thesis, Purdue University (1954).

(5) R. Hazeldine, *J. Chem. Soc.*, 2525 (1953).

(6) N. Bayliss and C. Brackenridge, *J. Am. Chem. Soc.*, **77**, 3959 (1955).

(7) H. Ungnade and L. Kissinger, *J. Org. Chem.*, **22**, 1088 (1957).

(8) G. Kortum, *Z. Electrochem.*, **47**, 55 (1941).

either from a 1:1 complex formation with the solvent or from a direct physical perturbation.

In this investigation the ultraviolet spectra of the series of dinitroparaffins prepared were observed in both 95% ethanol (Fig. 1) and in dioxane (Fig. 2). The molar absorbtivities of these compounds were approximately twice as great as those reported for similar mononitroparaffins, indicating that the nitro groups absorb independently with little or no interaction in the molecule. Both bathochromic and hyperchromic shifts were observed with increasing chain length in the series. Less solvent perturbation occurs with secondary nitroparaffins than with similar primary compounds. No absorption band was observed near 380 mμ when ethanol was used as solvent and therefore it appears that no ionization of these compounds in the solvents studied occurs.[8] Thus the α,ω-dinitroalkanes are considerably weaker acids than either nitromethane or the *gem*-dinitro compounds.

In the case of *gem*-dinitroparaffins, the molar absorptivity is increased by the active solvents to the extent that the 280 mμ band was completely submerged.[7] With this series of α,ω-dinitroparaffins, the molar absorptivities were increased only slightly (9–10 absorptivity units) when dioxane was employed as solvent. Of those compounds examined, 1,3-dinitropropane appears to be the strongest acid in the series. This would indicate that solvent perturbation in the case of *gem*-dinitro compounds (stronger acids) involves a considerable amount of 1:1 complex formation. However, the small amount of solvent perturbation of α,ω-dinitroparaffins is probably the result of active solvent molecules forming a cage in close proximity to and surrounding the solute (a physical perturbation).

Electrolyses of aqueous solutions of the *aci*-salt of 1,6-dinitrohexane using a procedure described by Bahner were unsuccessful in an attempt to prepare 1,2-dinitrocyclohexane via oxidative ring closure.[9]

EXPERIMENTAL

The dinitroalkanes (Table I) were prepared essentially by the modified Victor Meyer procedure.[10] A representative procedure is described for the preparation of 1,6-dinitrohexane.

1,6-Dinitrohexane. To 1.5 l. of freshly distilled dimethylformamide at 0° were added, with stirring, 180 g. (3.0 mol.) of dry urea, 180 g. (2.61 mol.) of dry sodium nitrite, and 146.4 g. (0.6 mol.) of redistilled 1,6-dibromohexane. The mixture was allowed to stir at 0° for 90 min. after which time 160 g. (1.27 mol.) of anhydrous phloroglucinol was added to scavenge the nitrite esters formed. The reaction mixture was allowed to warm to room temperature over a period of 24 hrs. The mixture was then poured into 1 l. of crushed ice and extracted with methylene chloride. The extracts were washed with water and a saturated salt solution, and then dried. The solvent was removed under reduced pressure and the residual liquid was fractionally distilled, b.p. 100–103°/0.3 mm. The distillate recrystallized from absolute methanol at −78°.

1,6-Diiodo-1,6-dinitrohexane. To a cold solution of 8.4 g. (0.38 mol.) of the disodium salt of 1,6-dinitrohexane, (prepared from the reaction of 1,6-dinitrohexane with sodium methoxide in methanol) in 75 ml. distilled water was added a cold solution of 11.4 g. (0.07 mol.) sodium iodide and 19.2 g. (0.07 mol.) iodine in 100 ml. water.[11] Decolorization of the iodine solution was instantaneous and was accompanied by the formation of a light yellow finely divided precipitate. The precipitate was removed by filtration and washed with a cold solution of sodium iodide and several portions of water to yield 10.4 g. (64%) of impure 1,6-diiodo-1,6-dinitrohexane. The product was recrystallized from petroleum ether (30–60°), from ethanol-water and from carbon tetrachloride to yield pure product, m.p. 68.5–69.5°. The compound gave a positive qualitative test for iodine.

Anal. Calcd. for $C_6H_{10}N_2O_4I_2$: C, 16.83; H, 2.36. Found: C, 16.70; H, 2.21.

Ultraviolet absorption spectra. The ultraviolet absorption spectra were determined for freshly prepared $2–3 \times 10^{-2}$ molar solutions in purified solvents with a Cary Model 11 recording spectrophotometer. Cell corrections, determined with pure solvent, were subtracted from the absorbancy values.

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[9] C. Bahner, U. S. patent **2,485,803**, Oct. 25, 1949; *Chem. Abstr.*, **44**, 2876 (1950).

[10] N. Kornblum, H. Larson, R. Blackwood, D. Mooberry, E. Eliveto, and G. Graham, *J. Am. Chem. Soc.*, **78**, 1497 (1956).

[11] L. Seigle, Ph.D. Thesis, Purdue University (1939).

[12] J. Kispersky, H. Hass, and D. Holcomb, *J. Am. Chem. Soc.*, **71**, 516 (1949).

Structure and Spectra. I. Ultraviolet Absorption Spectra of 2,4-Dinitrophenylhydrazones of Aliphatic Dienones and Styryl Ketones

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The ultraviolet absorption spectrum of 2,4-dinitrophenylhydrazones of saturated and α,β-unsaturated carbonyl compounds is characterized by two distinct bands at 250–260 mμ and 350–400 mμ. The absorption of the 2,4-dinitrophenylhydrazones of styryl ketones, where the α,β-olefinic bond is conjugated to an aryl moiety, has now been examined. In every case a third maximum was observed at 300–310 mμ, not as a shoulder on the two other bands, but as a separate band, usually having an absorption intensity lower than the other two.

The spectra of some 2,4-dinitrophenylhydrazones of styryl ketones are reported in Table I, and some examples are described in Fig. 1. It is seen that the K-bands fall in the region 390–400 mμ, which is beyond that found by Braude and Jones[1] for

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[1] E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 498 (1945).