portant in determining the ease of oxidation and the yield of ester.

The retention of the neopentyl and neophyl skeletal systems in the product esters, with no indication of contamination by either tert-amyl or benzyldimethylcarbinyl acetates, incidentally affords support for the concerted (non-carbonium ion) type mechanism usually ascribed to this reaction.[4]

EXPERIMENTAL

Analyses were performed by Galbraith Laboratories, Knoxville, Tenn. The infrared spectra were determined on liquid samples on Perkin-Elmer Model 21 Infrared Spectrophotometers by Miss E. Godar of this laboratory and by the Anderson Physical Laboratory, Champaign, Ill. Melting and boiling points are uncorrected.

Materials. Trifluoroacetic anhydride was commercial material (Halogen Chemicals), used as received. *Hydrogen peroxide* (90%) was generously supplied by the Becco Chemical Division of the Food Machinery and Chemical Corp., Buffalo, N. Y. *Neopentyl methyl ketone* was prepared as reported[5] by the dichromate oxidation of diisobutylene (Eastman) [44% yield, b.p. 124–127°, n_D^{20} 1.404, d_4^{20} 0.800, 2,4-dinitrophenylhydrazone m.p. 97° (lit.[6] m.p. 100°)]. *Neophyl methyl ketone* was prepared as reported[7] by the addition of mesityl oxide to benzene under aluminum chloride catalysis (61% yield, b.p. 61–62° at 1 mm., n_D^{20} 1.5115, d_4^{20} 0.973 [lit.[7] b.p. 134° at 22 mm., d_{25}^{25} 0.972)]. The 2,4-dinitrophenylhydrazone was prepared in the usual fashion, m.p. 98.5–99°.

Anal. Calcd. for $C_{18}H_{20}N_4O_4$: N, 15.71. Found: N, 15.56.

Authentic *neopentyl acetate* was obtained by the esterification of commercial neopentyl alcohol (Aldrich) in the usual manner with acetic acid and a trace of sulfuric acid [50% yield, b.p. 127°, n_D^{20} 1.390, d_4^{20} 0.855 (lit.[8] b.p. 127°, n_D^{20} 1.3893, d_4^{20} 0.8544)]. Authentic *neophyl acetate* was similarly obtained from neophyl alcohol[9] (60% yield, b.p. 105° at 5 mm., n_D^{20} 1.4959, d_4^{20} 1.008).

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.38. Found: C, 75.17; H, 8.47.

The oxidation of neopentyl methyl ketone. A solution of peroxytrifluoroacetic acid was prepared by the dropwise addition of trifluoroacetic anhydride (37.8 g., 25.4 ml., 0.18 mole) to an ice cold solution of hydrogen peroxide (90%, 5.1 g., 4.1 ml., 0.15 mole) in methylene chloride (50 ml.). This solution was added dropwise over a 45-min. period to a stirred suspension of neopentyl methyl ketone (11.4 g., 0.1 mole) in methylene chloride (75 ml.) containing dry, finely powdered disodium hydrogen phosphate (65 g.). The exothermic reaction was controlled by the rate of addition and was completed by refluxing for 2 hr. after the addition was completed. The customary[2] work-up of the reaction mixture gave pure neopentyl acetate (5.25 g., 40% yield, b.p. 127–29°, n_D^{20} 1.390, d_4^{20} 0.863). The material gave a positive hydroxamic acid test for esters.

The infrared spectra of this product and authentic neopentyl acetate (see above) were identical, with indicative bands at 5.75s mμ (saturated ester $C{=}O$), 6.76m mμ (CH_2), 7.27s mμ ($C_3{\equiv}C$) and 8.05s mμ (acetate C—O—).

The oxidation of neophyl methyl ketone. A solution of peroxytrifluoroacetic acid was prepared as before, using double those amounts, and added as before to a solution of neophyl methyl ketone (35.2 g., 0.2 mole) in methylene chloride (150 ml.) containing dry, finely powdered disodium hydrogen phosphate (130 g.). Treatment of the reaction mixture in the usual fashion[2] gave neophyl acetate contaminated with much unchanged ketone (20 g., b.p. 90–100° at 4 mm., n_D^{20} 1.500, d_4^{20} 0.989). Purification was effected by means of Girard's reagent T in the usual manner [10] and furnished pure neophyl acetate [11.0 g., 28.5% yield (38.5% yield based on consumed ketone), b.p. 89–90° at 2 mm., n_D^{20} 1.4960, d_4^{20} 1.003]. This material was ketone free and gave a positive hydroxamic acid test for esters.

The infrared spectra of this product and authentic neophyl acetate (see above) were identical, with indicative bands at 5.76s mμ (saturated ester $C{=}O$), 6.75m mμ (CH_2), 7.26s mμ ($C_3{\equiv}C$) and 8.00–8.16s mμ (acetate C—O—), along with the expected peaks associated with aromatic unsaturation and mono-substitution.

Acknowledgment. We thank Miss E. Godar for certain of the infrared spectral measurements.

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(4) *Cf.* footnote 2 for leading references.

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Configuration of Two Dinitroölefins

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Work by Freeman and Emmons[2] on the addition of dinitrogen tetroxide to acetylenes led them to assign *cis* and *trans* configurations to isomers of two pairs of dinitroölefins. Through calculations of dipole moments from dielectric constant measurements on two of these same compounds we can add evidence to confirm their assignment. Dipole moments of 5.79 D and 5.16 D were obtained for 3,4-dinitro-3-hexene, m.p. 31–32°, and 2,3-dinitro-2-butene, m.p. 28.0–28.5°, respectively, the isomers obtained from treatment of 1-chloro-1-nitro alkanes with alkali. Since the dipole moment of a nitro group in an alkane is about 3.3 D, the measurement constitutes strong evidence for the *cis* configuration in these compounds. Courtauld models of the *cis* isomers suggest that the two nitro groups may not be co-planar with the double bond. There is room for this interpretation in the values of the dipole moments, which are less than expected for *cis* nitro groups coplanar with the double bond.

A distorted *cis* structure for the two compounds is

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(1) Taken from the M.S. thesis of T. E. Mead, Brown University, 1957.

(2) J. P. Freeman and W. D. Emmons, *J. Am. Chem. Soc.*, **79**, 1712 (1957).

also consistent with the infrared spectra. A medium band at 1676 cm.$^{-1}$ in 3,4-dinitro-3-hexene and at 1686 cm.$^{-1}$ in 2,3-dinitro-2-butene was attributed in this laboratory to a C═C stretching vibration, a higher frequency than is common for this band. Two large nitro groups on either end of a double bond in the *cis* form would certainly twist the double bond and could cause an enhancement of its C═C frequency and an increase in its intensity.[3] This is in essential agreement with the interpretation given by Freeman and Emmons[2] for the two bands they found at 1667 cm.$^{-1}$ and 1676 cm.$^{-1}$ in the same compounds.

Additional evidence for a distorted *cis* configuration lies in a study of the ultraviolet spectra of the two dinitroölefins. The spectra of 2,3-dinitro-2-butene (λ_{max}, 219 mμ and ϵ, 5980) and 3,4-dinitro-3-hexene (λ_{max}, 219 mμ and ϵ, 5290) were very similar to the spectrum of 2-nitro-1-butene (λ_{max}, 223 mμ and ϵ, 1030). Actually the maximum for the K-bands (N→V) transitions appeared at only slightly lower wave lengths than in mononitroolefins.

The results in the ultraviolet measurements can be justified in the following way. K-bands for triply conjugated systems usually appear near 260 mμ but systems terminating in oxygen atoms are exceptional in that a shift to lower wavelengths occurs. An example is diacetylacetylene whose K-band appears at 236 mμ;[4] only one carbonyl group appears to enter into conjugation. A second argument rests on the statement that the wave length, λ, is proportional to the distance between charge centers in the excited state. In the *cis* configuration the separation of formally charged atoms is smaller than in the *trans* configuration. A third argument depends on the steric requirements of the conjugated system. In a *cis* structure steric inhibition of co-planarity should cause a hypsochromic effect,[5] that is, a shift in λ_{max} to lower wave lengths, as observed.

EXPERIMENTAL

cis-2,3-Dinitro-2-butene and cis-3,4-dinitro-3-hexene. The two dinitroölefins, *cis*-2,3-dinitro-2-butene, m.p. 28.0–28.5°, and *cis*-3,4-dinitro-3-hexene, m.p. 31–32°, were prepared by the method recently described in *Organic Syntheses*.[6] Infrared bands (melted on NaCl disks) for 2,3-dinitro-2-butene, cm.$^{-1}$: 3597 (m), 3003 (m), 1689 (m), 1558 (s), 1538 (s), 1435 (s), 1389 (s), 1346 (s), 1337 (s), 1217 (w), 1114 (m), 1028 (w), 969 (w), 885 (s), 821 (s).

For 3,4-dinitro-3-hexene, cm.$^{-1}$: 3067 (m), 3030 (shoulder), 1675 (w), 1555 (s), 1538 (s), 1458 (s), 1429 (s), 1348 (s), 1269 (w), 1202 (w), 1120 (m), 1056 (m), 959 (w), 896 (w), 815 (s), 804 (s).

Dipole moments of cis-2,3-dinitro-2-butene and cis-3,4-dinitro-3-hexene. Dielectric constants of benzene and carbon tetrachloride (Baker and Adamson Co., Inc., ACS Reagent Grade) solutions of the two dinitroölefins were determined at 100 kc/sec. using a capacitance-conductance bridge previously described.[7] The benzene was purified by the method of Nace and Turner.[8] Cell constants were calculated from capacitance measurements on carbon tetrachloride and cyclohexanol whose dielectric constants are accurately known.[9] The molar polarization and the dipole moments were then obtained by the method well described by Nace and Turner[8] except that the solute distortion polarization was taken as the molar refraction, calculated from atomic refraction values.

The following dipole moments were obtained: *m*-dinitrobenzene in benzene, 3.88 D[10]; 2,3-dinitro-2-butene in benzene, 5.16; in carbon tetrachloride, 5.16; 3,4-dinitro-3-hexene in benzene, 5.76; in carbon tetrachloride, 5.79.

TABLE I

MOLAR POLARIZATIONS IN CCl$_4$

Molality	Capacitance (Measured)	ϵ'	P_{12}
	2,3-Dinitro-2-butene at 25.2°		
.00	54.244	2.235	...
.01	55.523	2.291	29.127
.03	57.759	2.388	30.615
.05	59.874	2.481	31.987
.07	61.924	2.571	33.258
.09	63.957	2.660	34.463
	3,4-Dinitro-3-hexene at 26.0°		
.00	54.192	2.232	...
.01	55.703	2.298	29.263
.03	58.632	2.427	31.246
.05	61.638	2.558	33.148
.07	64.782	2.696	35.038
.09	67.862	2.830	36.771

Ultraviolet spectra of 2,3-dinitro-2-butene and 3,4-dinitro-3-hexene. Ultraviolet spectra were obtained with a Beckman Model DU Spectrophotometer in the region 210–320 mμ on 2,3-dinitro-2-butene and 2-nitro-1-butene and 210–350 mμ on 3,4-dinitro-3-hexene in 95% ethanol. The experimental data are given in the discussion above.

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