were not characterized further, but, to verify that aromatic acetoxy compounds have longer retention times than bromo compounds, a test mixture was run consisting of 1-methylnaphthalene, 1-bromo-4-methylnaphthalene, and 1-acetoxy-4-methylnaphthalene. The difference in retention time between the bromo and acetoxy derivatives of 1-methylnaphthalene is very similar to that of the derivatives of 1,5-dimethylnaphthalene. Furthermore, when the response factors of the monomethyl compounds were used to calculate weight per cent of a kinetic run, the weight of bromo to acetoxy compounds was found to be 56.9 to 43.1%, in good agreement with the ratio given above.

In the bromination of 2,3-dimethylnaphthalene, a 97.4% yield of 1-bromo-2,3-dimethylnaphthalene was obtained. It was characterized by a comparison with the retention time of an authentic sample, which was prepared according to a literature procedure and had mp 61.8–62.8° (lit.[22] mp 63–64°). The 2.6% constitute another monobromo isomer, most likely the 5 isomer (1-bromo-6,7-dimethylnaphthalene). Material balances on three runs were 97.9, 68.8, and 93.5%. Chromatography of the total reaction product on an SE-30 column showed that no acetoxy products were present. No dibromo substitution products were detected in the bromination of either hydrocarbon.

(22) R. T. Arnold and R. W. Liggett, *J. Amer. Chem. Soc.*, **64**, 2875 (1942).

The gas chromatographic analyses were done on a programmed temperature gas chromatograph (F & M Scientific Corp., Model 720). For the separation of the bromo isomers a 4 ft × 0.25 in. column of 5% Apiezon L-5% Bentone 34 on 80–100 Diatoport S was used. Hydrocarbons were analyzed on a 2 ft × 0.25 in. column of Carbowax 20M on 80–100 Diatoport S and acetoxy compounds on a 6 ft × 0.25 in. column of 5% SE-30.

The infrared spectra were recorded in chloroform on a Perkin-Elmer Infracord, Model 137, and the nmr spectra on a Varian Model A-56/60-A spectrometer.

Registry No.—1,5-Dimethylnaphthalene, 571-61-9; 2-bromo-1,5-dimethylnaphthalene, 15095-53-1; 4-bromo-1,5-dimethylnaphthalene, 15095-54-2; 4-bromo-1,5-dimethylnaphthalene picrate, 15153-26-1.

Acknowledgment.—This work was supported by National Science Foundation Grant GP-4986, which is gratefully acknowledged. We are also glad to acknowledge a National Science Foundation Research Instrument Grant (GP-5431) for the purchase of a nuclear magnetic resonance spectrometer.

Reactions of Conjugated Nitro Olefins with Phosphoranes and with Dimethylsulfoxonium Methylide to Give Ylides and Nitrocyclopropanes, Respectively[1a]

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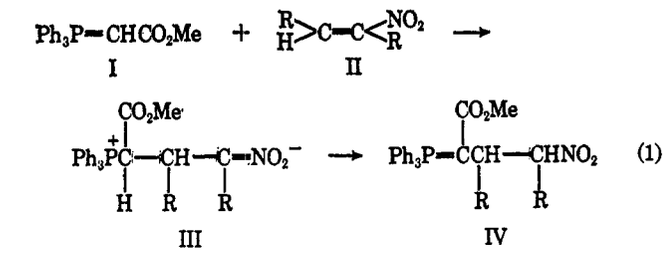
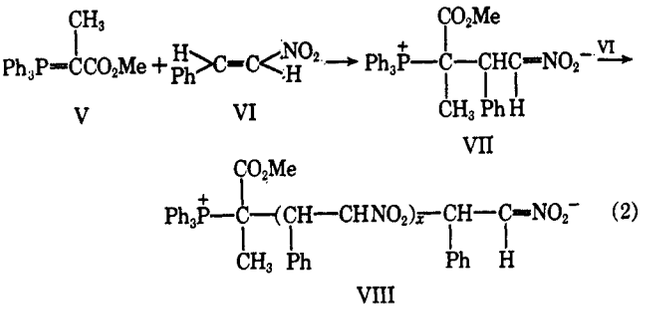
Carbomethoxymethylenetriphenylphosphorane (I) and conjugated nitro olefins (II) react with subsequent proton transfer to give phosphorus ylides, carbomethoxynitroalkylidenetriphenylphosphoranes (IV). The structures of IV were established from their infrared and ultraviolet absorptions. Chemical evidence for the structure of a typical phosphorane (X) was obtained by its bromination and subsequent regeneration by aqueous sodium carbonate. Methylenetriphenylphosphorane (XIV) and dimethylsulfoxonium methylide (XVIII) react with conjugated nitro olefins to yield nitrocyclopropanes; XVIII is the much more efficient and convenient reagent. The spectral properties of various nitrocyclopropanes are described.

Carbomethoxymethylenetriphenylphosphorane (I)[2] has been presently found to add to various conjugated nitro olefins (II, Table I) at 90° in hydrocarbon solvents with subsequent proton transfer (eq 1)



(1)

to give carbomethoxynitroalkylidenetriphenylphosphoranes (IV) efficiently.[3] Reaction of I and II or thermolysis of IV resulting in expulsion of triphenylphosphine to give nitrocyclopropanes, isoxazoline oxides, or related products could not be effected advantageously. Carbomethoxyethylidenetriphenylphosphorane (V)[2] reacts with β-nitrostyrene (VI) to give multiple adducts (VIII, eq 2). Phosphonium nitronates (VII) which do not self-neutralize to nitroalkylphosphoranes (IV) thus may continue Michael addition to conjugated nitro olefins.[3]



(2)

The phosphorus ylides (IV) prepared by the new method are stable greenish white solids which can be recrystallized conveniently from hydrocarbons and from ethyl acetate. The structures of the products as phosphoranes (IV) are assigned from their infrared absorptions (Table I) for nitro (6.48–6.51 μ)[4] and phosphoranocarbonyl (6.13–6.23 μ) groups and from

(1) (a) This research was supported by the Office of Naval Research. (b) To whom inquiries should be addressed.

(2) (a) G. Wittig and G. Geissler, *Ann.*, **580**, 44 (1953); (b) O. Isler, H. Guttman, M. Montavon, R. Ruegg, G. Ryser, and P. Zeller, *Helv. Chim. Acta*, **40**, 1242 (1956).

(3) H. J. Bestmann and F. Seng [*Angew. Chem.*, **74**, 154 (1962)] have reported a similar reaction in that I reacts with methyl benzoylacrylate to give triphenylphosphine and [(1-carbomethoxy-2-benzoyl)ethyl]carbomethoxymethylene.

(4) J. F. Brown Jr., *J. Amer. Chem. Soc.*, **77**, 6341 (1955).

TABLE I

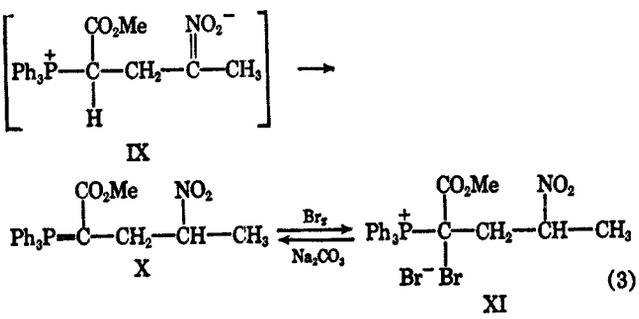
REACTION OF CARBOMETHOXYMETHYLENETRIPHENYLPHOSPHORANE (I) WITH CONJUGATED NITRO OLEFINS (II)

Nitro olefins	Phosphoranes, IV[b]	Mp °C[a]	% yield[b]	Molecular formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N	Ir absorption,[c] μ >C=O	Ir absorption,[c] μ NO_2
$H_2C{=}C(CH_3)NO_2$	$Ph_3P{=}C(CO_2CH_3)CH_2CH(CH_3)NO_2$	162–164	57	$C_{24}H_{24}NO_4P$	68.50	5.70	3.32	68.21	5.71	3.44	6.13	6.51[d]
$CH_3CH{=}CHNO_2$	$Ph_3P{=}C(CO_2CH_3)CH(CH_3)CH_2NO_2$	164–166	33	$C_{24}H_{24}NO_4P$	68.50	5.70	3.32	68.26	5.55	3.38	6.14	6.49[e]
$CH_3CH{=}C(CH_3)NO_2$	$Ph_3P{=}C(CO_2CH_3)CH(CH_3)CH(CH_3)NO_2$	193.5–195.5	33	$C_{25}H_{26}NO_4P$	68.96	6.00	3.22	68.81	6.12	3.30	6.13	6.51[f]
$PhCH{=}CHNO_2$	$Ph_3P{=}C(CO_2CH_3)CHPhCH_2NO_2$	180–181	23	$C_{29}H_{26}NO_4P$	72.01	5.38	2.90	71.95	5.48	2.85	6.17	6.48[g]
$PhCH{=}C(CH_3)NO_2$	$Ph_3P{=}C(CO_2CH_3)CHPhCH(CH_3)NO_2$	204–207	49	$C_{30}H_{28}NO_4P$	72.43	5.63	2.90	72.15	6.05	2.67	6.17	6.50[h]
$PhCH{=}C(Ph)NO_2$	$Ph_3P{=}C(CO_2CH_3)CHPhCHPhNO_2$	173–174	28	$C_{35}H_{30}NO_4P$	75.13	5.37	2.50	75.16	5.56	2.66	6.14	6.48[i]
$(C_4H_3O)CH{=}CHNO_2$)	$Ph_3P{=}C(CO_2CH_3)CH(C_4H_3O)CH_2NO_2$	184.5–185.5	47	$C_{27}H_{24}NO_5P$	68.50	5.08	2.96	68.76	5.24	3.24	6.23	6.48[j]

[a] The phosphoranes melt with decomposition. [b] The actual yields are considerably higher (60–80%); the values reported are those for the analytical samples. [c] Determined in potassium bromide pellets. [d] Uv, λ_{max} (ϵ_{max}) taken in 95% ethanol: 225 (38,700), 261 (5050), 266.5 (5050), and 273.5 (4430). [e] Uv, λ_{max} (ϵ_{max}) taken in 95% ethanol: 225 (37,600), 261 (5770), 266 (5652), and 273 (4800). [f] Uv, λ_{max} (ϵ_{max}) taken in 95% ethanol: 225 (32,222), 260.5 (5160), 267 (5040), and 273.5 (4200). [g] Uv, λ_{max} (ϵ_{max}) taken in 95% ethanol: 225 (39,190), 261 (5787), 266 (6000), 273 (5545), and 304–311 (5400). [h] Uv, λ_{max} (ϵ_{max}) taken in 95% ethanol: 223 (42,666), 262 (5636), 267 (6609), 274 (6913), and 309–312 (10,363). [i] Uv, λ_{max} (ϵ_{max}) taken in 95% ethanol: 223 (38,000), 261 (6200), 267 (5900), and 273 (4800). [j] Uv, λ_{max} (ϵ_{max}) taken in 95% ethanol: 225 (28,400), 260 (4500), 266 (4400), 273 (3700), and 347 (6800). [k] Respective registry no.: 15267-29-5; 15267-30-8; 15267-22-8; 15267-32-0; 15267-33-1; none.

the similarities of their ultraviolet absorptions (Table I) in 95% ethanol (λ_{max} 223–224 (ϵ_{max} 28,400–42,600), 260–262 (1300–6200), 266–267 (1700–6600), and 273 (1400–6900))[5] to that of I (λ_{max} 223–225 (ϵ_{max} 21,200), 260 (1300), 266 (1700), and 272.5 (1400)) and V (λ_{max} 224 (ϵ_{max} 32,100), 260.5 (1800), 266 (2300), and 273 (1900)). If the products were the dipolar adducts III, infrared absorption for the nitronate and carbonyl groups would occur intensely at ~6.2 and 5.7–5.8 μ, respectively, and there should be strong ultraviolet absorption for alkanenitronate groups[6] at 223–234 mμ (9000–11,000) or for arylmethanenitronate ions[6] at 291 mμ (12,000).

The product of reaction of I and 2-nitropropene, methyl 4-nitro-2-(triphenylphosphoranylidene) valerate, was demonstrated chemically (eq 3) to be an

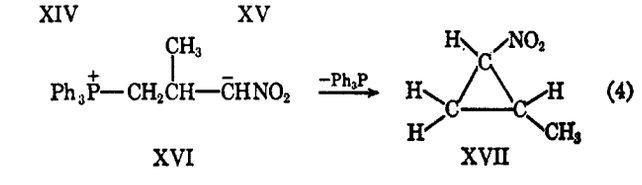


(3)

ylide (X) rather than a phosphonium salt (IX) upon (eq 1) its bromination to a bromophosphonium bromide (XI) exhibiting carbonyl and nitro absorptions at 5.81 and 6.48 μ, respectively, and (eq 2) reaction of XI with aqueous sodium carbonate resulting in regeneration of X. Bromination of the phosphonium nitronate (IX) is expected to occur at the nitronate group. No significant shift in the wave length of the carbonyl absorption would be anticipated as a result of bromination of IX since the carbonyl groups in the reactant and the product should have similar stretching vibrations. Also a shift in the absorption of the nitro group to a lower wave length (~6.37 μ) would be expected upon bromination of IX because of the electron-withdrawing ability of bromine in α-bromo-α-nitro structures.

The utility of methyl 3-methyl-4-nitro-2-(triphenylphosphoranylidene)butyrate (XII) and methyl 4-nitro-3-phenyl-2-(triphenylphosphoranylidene)butyrate (XIII) as ylide reagents for activated aldehydes was investigated. Reactions of XII and XIII with *m*-nitrobenzaldehyde occur slowly to yield the common product, methyl *m*-nitrocinnamate. It is apparent that XII and XIII undergo proton transfer reversal and reverse Michael addition (eq 1) to generate I and the respective nitro olefins. Reaction of *m*-nitrobenzaldehyde and I then yields methyl *m*-nitrocinnamate.

Methylenetriphenylphosphorane (XIV) reacts with 1-nitropropene (XV, eq 4) and with 2-nitro-2-butene in anhydrous dimethyl sulfoxide at 10° to give 2-methyl-1-nitrocyclopropane (XVII) and 1,2-dimethyl-1-nitrocyclopropane[7] in poor (5–7%) yields. Addition of XIV to the nitro olefins occurs with expulsion of triphenylphosphine; however there is extensive Michael polymerization of the nitro olefins under these conditions[8] along with conversion of the phosphorus-containing materials into triphenylphosphine oxide.



(4)

Dimethylsulfoxonium methylide (XVIII)[9] in anhydrous dimethyl sulfoxide is an effective reagent for converting conjugated nitro olefins (II, Table II) into

(5) (a) Aliphatic nitro compounds exhibit a principal absorption band at 270–280 mμ; the absorption is of low intensity (ε *ca.* 15–30).[4] (b) H. E. Ungnade and R. A. Smiley, *J. Org. Chem.*, **21**, 993 (1956).

(6) (a) F. T. Williams, Jr., P. W. K. Flanagan, W. J. Taylor, and H. Shechter, *J. Org. Chem.*, **30**, 2674 (1965). (b) A. Hantzsch and K. Voigt, *Ber.*, **45**, 85 (1912). (c) The intermediate, III, from I and α-nitrostilbene is an arylmethanenitronate.

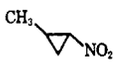
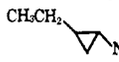
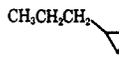
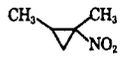
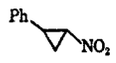
(7) 1-Butylidenetriphenylphosphorane and 9-*n*-butylidenefluorene yield spiro(2,3-dipropylcyclopropane-1,9-fluorene); R. Mechoulam and F. Sondheimer, *J. Amer. Chem. Soc.*, **80**, 4386 (1958).

(8) Ethylidenetriphenylphosphorane in dimethyl sulfoxide results in extensive polymerization and decomposition of β-nitrostyrene, 1-nitropropene and 2-nitro-1-butene, respectively.

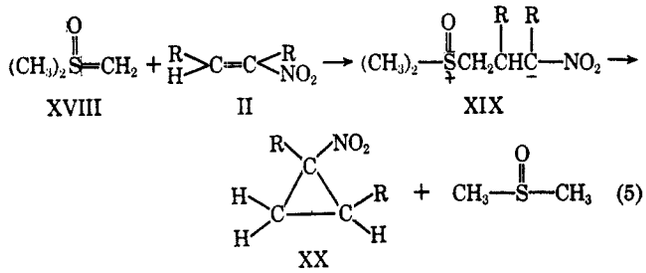
(9) E. J. Corey and M. Chaykovsky, *ibid.*, **84**, 867, 3782 (1962).

TABLE II

REACTIONS OF DIMETHYLSULFOXONIUM METHYLIDE (XVIII) WITH CONJUGATED NITRO OLEFINS (II)

Nitro olefins	Nitrocyclopropanes	Bp, °C (mm)	% yield[a]	Molecular formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N	Ir absorption,[b] μ NO_2	Uv absorption,[c] mμ (ϵ_{max})
$CH_3CH{=}CHNO_2$		69 (30)	31	$C_4H_7NO_2$	47.52	6.93	13.87	47.67	6.71	14.00	6.48, 7.34	219 (6650)
$CH_3CH_2CH{=}CHNO_2$		62 (10)	40	$C_5H_9NO_2$	52.27	7.82	12.17	52.65	7.79	12.35	6.48, 7.33	219 (6950)
$CH_3CH_2CH_2CH{=}CHNO_2$		76 (11)	43	$C_6H_{11}NO_2$	55.81	8.52	10.85	55.81	8.62	11.01	6.49, 7.33	219 (6445)
$CH_3CH{=}C(CH_3)NO_2$		70 (20)	37	$C_5H_9NO_2$	52.27	7.82	12.17	52.50	7.60	12.35	6.51, 7.39	216 (6236)
$Ph{-}CH{=}CHNO_2$		85–87 (1)	44	$C_9H_9NO_2$	66.26	5.52	8.58	65.93	5.70	8.63	6.49, 7.34	213 (11,230); 252 (8230)

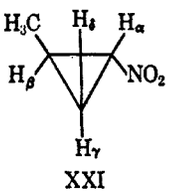
[a] The actual yields are much higher; the values reported are those for multiply distilled analytical samples. [b] Determined in potassium bromide pellets. [c] Determined in 95% ethanol.



XVIII II XIX XX (5)

substituted nitrocyclopropanes (XX) (eq 5).[10-12] The addition reactions are run preparatively by adding the nitro olefins to excess XVIII at 0–10°. The products are usually isolable and purifiable without complication. Conversion of 2-nitro-1-alkenes into nitrocyclopropanes is inefficient, however, because of polymerization of the nitro olefins by XVIII. The nitrocyclopropanes are colorless, pleasant liquids stable to storage, insoluble in aqueous bases,[13] and readily separable from their parent nitro olefins by distillation methods.

The α-nitro-β-substituted cyclopropanes prepared appear to have *trans* stereochemistry.[14] The structure of the product of reaction of XVIII and 1-nitro-1-propene (principally the *trans* isomer) is assigned as *trans*-2-methyl-1-nitrocyclopropane (XXI) on the



XXI

basis of its nmr for two deshielded cyclopropyl hydrogens between τ 8.0 and 8.35 (H_β and H_γ, multiplet, area 1.93),[15a] a methyl group[15b] which is not deshielded and which integrates with cyclopropyl hydrogen (H_δ, not deshielded) between 8.70 and 9.06 (multiplet, area 4.25), and cyclopropyl hydrogen at 5.95 (H_α, quintet, area 1.0) on carbon bearing the nitro group.[15c] Chemical evidence for the stereochemical assignment was obtained in that the nitrocyclopropane is not separated into geometric isomers by gas chromatography on GF-1 (Dow Corning Co.) Chromsorb,[16] and reduction by iron and hydrochloric acid[17] gives 2-methyl-1-cyclopropylamine whose gas chromatographic properties are essentially identical with that of *trans*-2-methyl-1-cyclopropylamine (XXII) prepared as indicated in eq 6 (see Experimental Section) and

(10) The yields listed in Table II are for highly purified nitrocyclopropanes. The actual yields are considerably greater than those given.

(11) (a) XVIII reacts with α,β-unsaturated ketones,[11b] amides,[11c,d] nitriles,[11e] and sulfones[11f] to give cyclopropanes. (b) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1353 (1965); (c) P. T. Izzo, *J. Org. Chem.*, **28**, 1713 (1963); (d) B. Loev, M. F. Kormendy, and K. M. Snader, *Chem. Ind.* (London), 1710 (1964); (e) C. Kaiser, B. M. Trost, J. Beeson, and J. Weinstock, *J. Org. Chem.*, **30**, 3972 (1965); (f) W. E. Truce and V. U. Badiger, *ibid.*, **29**, 3277 (1964).

(12) It has been reported[11e] that β-nitrostyrene and XVIII do not give the corresponding nitrocyclopropane. In the present experiments the adduct, 1-nitro-2-phenylcyclopropane, is obtained.

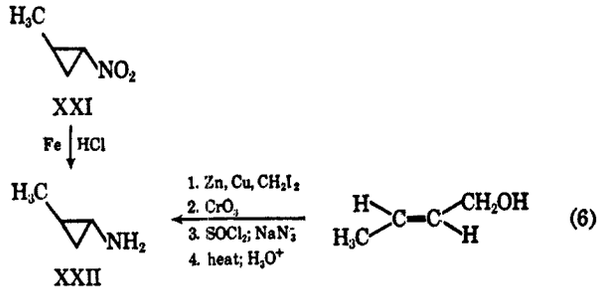
(13) The resistance of conversion of 2-methyl-1-nitrocyclopropane into its corresponding nitronate ion is also indicated by the observation that the ultraviolet absorption of the nitrocyclopropane is unchanged in homogeneous solution upon addition of excess base (also see ref 11e).

(14) Ethyl *trans*-cinnamate and *trans*-N,N-dimethylcinnamamide react with XVIII to give ethyl *trans*-2-phenylcyclopropanecarboxylate (98.9% stereoselective) and *trans*-N,N-dimethyl-2-phenylcyclopropanecarboxamide (100% stereoselective). Ethyl *cis*- and *trans*-2-phenylcyclopropanecarboxylates are not epimerized by the above reaction environment.[11e] *trans*-Cinnamonitrile and XVIII give a mixture of 78% *trans*- and 21% *cis*-2-phenylcyclopropanecarbonitriles.[11e] *trans*-Phenyl ω-styryl sulfone and XVIII yield only *trans*-1-phenyl-2-phenylsulfonylcyclopropane; *cis*-1-phenyl-2-phenylsulfonylcyclopropane is isomerized nearly quantitatively to its *trans* isomer under the conditions for addition of XVIII to the *trans*-sulfone.[11f]

(15) (a) Hydrogen *cis* to a nitro group in a nitrocyclopropane is expected to be highly deshielded. S. Ranganathan (Ph.D. Dissertation, The Ohio State University, Columbus, Ohio, 1962) observed that in 2-nitrospiro[cyclopropane-1,9′-fluorene] the τ values of the β and β′ hydrogens relative to the nitro group of the cyclopropane ring are 8.25 and 8.85, respectively. It is presumed that the β and β′ hydrogens are *cis* and *trans*, respectively, relative to the nitro group. (b) The nmr of shielded and unshielded methyl groups in the following cyclopropanes are 1-methyl- (τ 8.87) *trans*-2-phenylcyclopropane; 1-methyl- (τ 9.20) *cis*-2-phenylcyclopropane; 1-*cis*-2-dimethyl- (τ 8.87) *trans*-3-phenylcyclopropane; 1-*cis*-2-dimethyl- (τ 9.05) *cis*-3-phenylcyclopropane; and 1-*trans*-2-dimethyl- (τ 8.85 and 9.22) *trans*-3-phenylcyclopropane as given by J. P. Freeman [*J. Org. Chem.*, **29**, 1379 (1964)] and G. L. Closs and R. A. Moss [*J. Am. Chem. Soc.*, **86**, 4042 (1964)]. (c) Hydrogen on carbon attached to nitro groups in the present nitrocyclopropanes have τ values of 5.94–5.96. Protons on carbon bearing nitro groups in 2-nitropropane and 2-nitrobutane exhibit resonance at τ 5.33 and 5.48, respectively: Varian Associates NMR Spectra Catalog, Palo Alto, Calif., Spectrum No. 41 and 42.

(16) Such columns are effective for separating *cis*- and *trans*-alkylnitrocycloalkanes: G. E. Booth, private communication, 1966.

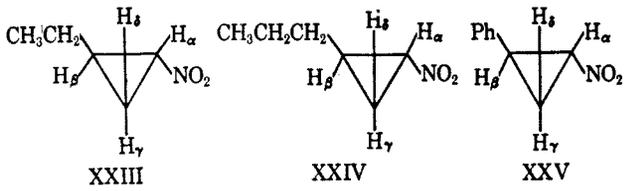
(17) Iron and hydrochloric acid reduce various *exo*- and *endo*-nitrobicycloalkanes to their corresponding amines without alteration of the initial stereochemistry: P. W. K. Flanagan, Ph.D. Thesis, The Ohio State University, Columbus, Ohio, 1957.



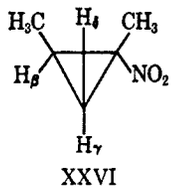
(6)

obtained as an authentic sample.[18] It is not yet clear whether XXI is formed from XVIII and 1-nitro-1-propene as a product of kinetic or thermodynamic control.

The products, XXIII, XXIV and XXV, from reaction of XVIII with 1-nitro-1-butene, 1-nitro-1-pentene, and *trans*-β-nitrostyrene, respectively, could not be separated effectively by gas chromatographic methods. The chromatographic traces were symmetrical upon passing each nitrocyclopropane through a variety of columns. Upon attempting to separate the products through long, highly polar, heated columns, there was distortion in the chromatographic responses. It could not be established, however, whether small amounts of initial geometrical isomers were present, whether there was some *cis–trans* isomerization during chromatography, or whether thermal decomposition of initial products led to unsymmetrical broadening of the gas chromatographic peaks.



The structure of XXIII is indicated as *trans*-2-ethyl-1-nitrocyclopropane from its nmr absorption for two deshielded ring protons (H_β and H_γ, multiplet, τ 8.28–8.40, area 2.10), methyl and ring protons (CH_3 and H_δ, multiplet, τ 8.85–9.20, area 4.1), which are not deshielded, alkylmethylene hydrogen (CH_2, sextuplet, τ 8.47–8.85, area 2.10), and hydrogen (H_α, quintet, τ 5.95, area 1.0) on carbon substituted by a nitro group. Similarly XXIV[19a] and XXV[19b] are assigned *trans* stereochemistries from their nmr properties. Although no attempts were made to separate by precision glpc techniques the adduct obtained from 2-nitro-2-butene and XVIII, it is clear from the nmr properties of the product that 1-*cis*-2-dimethyl-1-nitrocyclopropane (XXVI) must be at least the principal component.[20]



XXVI

The spectral properties of the nitrocyclopropanes prepared are of some note. The nitrocyclopropanes in which the nitro groups are at secondary carbon exhibit infrared absorption at 6.48–6.49 and 7.33–7.34 μ (Table II); their absorptions thus occur in general at longer wave lengths than do secondary aliphatic nitro compounds (6.38–6.47 and 7.22–7.35 μ).[21] The tertiary nitrocyclopropanes absorb at 6.51–6.52 and 7.39–7.41 μ and thus more closely approximate tertiary nitroalkanes (6.47–6.53 and 7.36–7.45 μ).[4,21] Ultraviolet absorption of the nitrocyclopropanes (Table II) occurs with intensity (ϵ_{max} ~6,000) in the 213–219 mμ range in 95% ethanol; since nitroalkanes and conjugated nitroalkenes exhibit $\pi \rightarrow \pi^*$ bands at ~210[22] and at 220–250 mμ (ϵ_{max} 3300–12,400),[22] it is apparent that there is an appreciable conjugative effect in the nitrocyclopropanes.

Experimental Section

Reagents and General Procedures.—1-Nitro-1-propene,[23a] 2-nitropropene,[23a,b] 1-nitro-1-butene,[23a] 2-nitro-2-butene,[23c] 1-nitro-1-pentene,[23a] β-nitrostyrene,[23d] 2-nitro-1-phenylpropene,[23e,f] α-nitrostilbene,[23d] 2-(2-nitrovinyl) furan,[23g] methylenetriphenylphosphorane (XIV),[2] ethylidenetriphenylphosphorane,[2] carbomethoxymethylenetriphenylphosphorane (I),[2] carbomethoxyethylidenetriphenylphosphorane (V),[2] and dimethylsulfoxonium methylide (XVIII)[9] were prepared by literature methods. In the subsequent experimental, typical procedures for reactions of conjugated nitroolefins with carbomethoxymethylenetriphenylphosphorane (I) and dimethylsulfoxonium methylide (XVIII) are described. These procedures are almost exact prototypes for the experiments summarized in Tables I and II.

Reaction of 2-Nitropropene and Carbomethoxymethylenetriphenylphosphorane (I).—2-Nitropropene (3.5 g, 0.04 mol), and phenylphosphorane (I) (13.4 g, 0.04 mol) were stirred in anhydrous toluene (80 ml) for 40 hr at 90–100°. The mixture was cooled and the toluene evaporated. Anhydrous ether (200 ml) was added to the dark brown residue, and the resulting solid (9.7 g, 57%) was filtered. Concentration of the ether filtrate afforded no additional product. Recrystallization of the solid from ethyl acetate yielded methyl 4-nitro-2-(triphenylphosphoranylidene) valerate (X), mp 161.5–163.5° dec.

Reaction of β-Nitrostyrene and α-Carbomethoxyethylidenetriphenylphosphorane.—β-Nitrostyrene (2.98 g, 0.02 mol) and this triphenylphosphorane (6.96 g, 0.02 mol) were heated at 90–100° in toluene (100 ml) for 24 hr. The mixture was cooled and concentrated and then ethyl ether (250 ml) was added. Filtration yielded β-nitrostyrene polymer (2.70 g) identified by its infrared absorption and its general properties.

(18) A gift from the Lakeside Laboratories, Inc., Milwaukee, Wis.

(19) (a) The nmr of XXIV indicates H_α (quintet, area 1.0) at τ 5.95, H_β and H_γ (multiplet, area 2.09) between 8.10 and 8.33, alkylmethylene hydrogens ($-CH_2CH_2-$, multiplet, area 4.20) at 8.33–8.86, and H_δ along with methyl protons (multiplet, area 4.14) at 8.86–9.24. (b) XXV exhibits resonance for H_α (quintet, area 1.0) at τ 5.96, H_β (deshielded, multiplet, area 1.06) at 7.07–7.52, H_γ (deshielded, multiplet, area 1.06) at 8.04–8.44, H_δ (quartet, area 1.06) at 8.60–9.02, and H on phenyl (area 4.86) at 2.80–3.24.

(20) The nmr of XXVI reveals methyl protons (singlet, area 2.80) on carbon bonded to the nitro group, H_β and H_γ (multiplet, area 1.80) at τ 8.10–8.33, methyl protons (multiplet, area 3.10) between 8.76–8.96, and H_δ (multiplet, area 1.0) at 9.14–9.33.

(21) (a) N. Kornblum, H. E. Ungnade, and R. A. Smiley, *J. Org. Chem.*, **21**, 377 (1956). (b) Reference 21a reports that 2-methyl-1-nitrocyclopropane absorbs at 6.50 μ and 7.36 μ and that conjugated nitro olefins exhibit absorption at 6.55–6.62 and 7.39–7.46 μ, respectively.

(22) (a) C. N. Rao, "Ultraviolet and Visible Spectroscopy," Butterworth and Co. Ltd., London, 1961, p 20; (b) E. A. Braude, E. R. H. Jones, and G. G. Rose, *J. Chem. Soc.*, 1104 (1947).

(23) (a) E. Schmidt and G. Rutz, *Ber.*, **61B**, 2142 (1928); (b) G. D. Buckley and C. W. Scaife, *J. Chem. Soc.*, 1471 (1947); (c) H. B. Hass, A. G. Susie, and R. L. Heider, *J. Org. Chem.*, **15**, 8 (1950); (d) J. Meisenheimer and F. Heim, *Ann.*, **355**, 275 (1907); (e) L. Bouveault and A. Wahl, *Compt. Rend.*, **134**, 1145 (1903); (f) L. Bouveault and A. Wahl, *Bull. Soc. Chim. Fr.*, [3] **29**, 519 (1903); (g) O. Moldenhauer, W. Irion, D. Mastaglio, R. P. Fluger, and H. Doser, *Ann.*, **583**, 50 (1953).

Concentration of the ether filtrate, and addition of 95% ethanol–ether (1:1, 200 ml) gave triphenylphosphine oxide (1.87 g), identified by its infrared properties. Further evaporation of the filtrate yielded a mixture of triphenylphosphine oxide and α-carbomethoxyethylidenetriphenylphosphorane.

Reaction of Methyl 4-Nitro-2-(triphenylphosphoranylidene) Valerate (X) with Bromine and Then Aqueous Sodium Carbonate.—Bromine (0.48 g, 0.003 mol) in carbon tetrachloride (10 ml) was added dropwise to methyl 4-nitro-2-(triphenylphosphoranylidene) valerate (X, 1.17 g, 0.0028 mol) in carbon tetrachloride (60 ml) at 25–30°. The resulting mixture was stirred 18 hr and then filtered to give bromophosphonium bromide XI (1.46 g, 91%) as a yellow solid, mp 116–120° dec. The infrared spectrum of XI contained strong absorption for carbonyl (5.81 μ) and aliphatic nitro (6.47 μ) groups. Attempts to recrystallize XI from hot absolute ethanol, benzene, carbon tetrachloride, chloroform, or pentane lead to its deterioration.

Compound XI (1.28 g, 0.0022 mol) was dissolved in water (150 ml) at room temperature, filtered, and treated with 10% aqueous sodium carbonate until the aqueous solution was basic. The mixture was filtered to give a green solid (0.51 g, 55%), identified as X by comparison of its infrared spectrum and its mixture melting point with that of initial material.

Reaction of Methyl 4-Nitro-3-phenyl-2-(triphenylphosphoranylidene)butyrate (XIII) and *m*-Nitrobenzaldehyde.—Compound XIII (3.19 g, 0.0066 mol) and *m*-nitrobenzaldehyde (1.00 g, 0.0066 mol) were heated at 100° in dry xylene for 40 hr. The mixture was then cooled and the xylene removed. Anhydrous ether (150 ml) was added to the orange residue and the resulting mixture filtered to give initial phosphorane (XIII, 1.94 g). The filtrate was concentrated *in vacuo* and then dissolved in hot 95% ethanol. Cooling gave methyl *m*-nitrocinnamate (0.34 g), mp 120–122°, identified by comparison of its infrared spectrum and its mixture melting point with those of an authentic sample.[24]

Reaction of Methylenetriphenylphosphorane (XIV) with 1-Nitro-1-propene.—A stirred mixture of sodium hydride (1.20 g, 0.05 mole) and dry dimethyl sulfoxide (75 ml) was heated at 65° under nitrogen until hydrogen was no longer evolved (~90 min). The pale yellow solution was cooled to 15° and then triphenylmethylphosphonium bromide (17.85 g, 0.05 mol) was slowly added. After additional stirring at room temperature for 30 min, the mixture was cooled to −10°; 1-nitro-1-propene (4.35 g, 0.05 mol) in dimethyl sulfoxide (25 ml) was added over a 30-min period, and the mixture was stirred at 75° for 6 hr and then at 25–30° for 12 hr. The mixture was poured on ice and extracted with ether. The ether extract was washed with water, dried over magnesium sulfate, and concentrated. The orange-black viscous residue was vacuum distilled through a short-path still to give an orange oil which on redistillation afforded 2-methyl-1-nitrocyclopropane (0.23 g, 5%) identified by comparison with a sample prepared from dimethylsulfoxonium methylide (XVIII) and 1-nitro-1-propene.[25]

Reaction of Dimethylsulfoxonium Methylide (XVIII) with 1-Nitro-1-pentene.—Trimethylsulfoxonium iodide (96.8 g, 0.44 mol) was added through Gooch tubing in 30 min to a stirred suspension of sodium hydride (10.56 g, 0.44 mol) in dimethyl sulfoxide (250 ml) under nitrogen. After stirring at room temperature for 4 hr, the mixture was cooled to 10° and 1-nitro-1-pentene (46.0 g, 0.4 mol) in dimethyl sulfoxide was added dropwise in 45 min.[26] The mixture was stirred at 50° for 4 hr and then at 25–30° for 12 hr, poured onto ice, and extracted with ether. The ether extracts were washed with water, dried over magnesium sulfate, and then concentrated at reduced pressure. The orange-red oil was vacuum distilled to give *trans*-2-nitro-1-*n*-propylcyclopropane (XXIV, 22.2 g, 43%) as a colorless liquid (Table II).

2-Methylcyclopropylcarbinol.—A mixture of crotyl alcohol (~80% *trans*, 20% *cis*, 18.0 g, 0.25 mole) and methylene iodide (83.8 g) was added in 2 hr to a stirred suspension prepared by dropwise addition of methylene iodide (10 g, total CH_2I_2, 0.35 mol) to zinc–copper couple[27] (32.7 g, 0.5 mol) in ethyl ether (100 ml). After the stirred mixture had refluxed 25 hr, the ether solution was slowly decanted into a mixture of ice and hydrochloric acid. The ether solution was separated, washed with ice–hydrochloric acid and then water, dried over potassium carbonate, and then concentrated. Distillation of the resulting oil gave 2-methylcyclopropylcarbinol (8.2 g, 38% yield), bp 128–130° (lit.[28] bp 133°). Vapor phase chromatography showed the reaction product to be a 80:20 mixture of *trans*- and *cis*-2-methylcyclopropylcarbinols.

2-Methylcyclopropanecarboxylic Acid.—2-Methylcyclopropylcarbinol (3.3 g, 0.04 mole) was added dropwise to a stirred solution of chromic oxide (15.5 g, 0.15 mol), sulfuric acid (13.6 ml), and water (45 ml) at 0–5°. The mixture was then stirred for 3 hr. The acid solution was extracted with ethyl ether; the ether extracts were dried, concentrated, and distilled to give 2-methylcyclopropanecarboxylic acid (2.4 g, 60% yield), bp 101–102° (22 mm) (lit.[28] bp 97–98° (17.6 mm)). The product upon vapor phase chromatography was found to be a mixture containing 80% of the *trans*- and 20% of the *cis*-2-methylcyclopropanecarboxylic acids.

2-Methylcyclopropylamine.—2-Methylcyclopropanecarboxylic acid (2.2 g, 0.02 mol) and thionyl chloride (10 ml) were stored for 24 hr at 25–30°. The excess thionyl chloride was then removed *in vacuo* to give 2-methylcyclopropanecarbonyl chloride (1.7 g). The acid chloride was dissolved in acetone (40 ml), cooled to 10°, and then treated dropwise with a solution of sodium azide (2.6 g, 0.04 mole) in water (8 ml). The mixture was stirred for 30 min and then poured into ice water (250 ml). The aqueous solution was extracted with ether, and the ether washings were dried over anhydrous magnesium sulfate and concentrated. The residual azide was added to dry toluene (30 ml), heated with steam for 2 hr, and concentrated to give 2-methylcyclopropyl isocyanate. The isocyanate was hydrolyzed in refluxing hydrochloric acid (50 ml) for 12 hr and concentrated *in vacuo* to yield crude 2-methylcyclopropylamine hydrochloride. The hydrochloride was dissolved in water (50 ml), made alkaline with 10% sodium hydroxide, and extracted with ether. The ether extract was dried and concentrated to give 2-methylcyclopropylamine whose infrared spectrum is essentially identical with that obtained for the product of reduction of *trans*-2-methyl-1-nitrocyclopropane (XXI).

Reduction of *trans*-2-Methyl-1-nitrocyclopropane (XXI).—Concentrated hydrochloric acid (8 ml) was added in 3 hr to a refluxing mixture of *trans*-2-methyl-1-nitrocyclopropane (XXI) (1.15 g, 0.011 mol) and iron dust (2.0 g, 0.036 g-atom) in water (20 ml). The mixture was then refluxed for 6 hr, cooled, made alkaline with aqueous sodium hydroxide (10%), and then filtered. The filtrate was extracted with ether; the combined ether extracts were dried over magnesium sulfate and concentrated. The infrared spectrum of the product (XXII) was identical with that of authentic *trans*-2-methyl-1-cyclopropylamine. Its gas phase chromatographic properties revealed that the principal component is identical with that from Curtius reaction of *trans*-2-methylcyclopropanecarboxylic acid.

Registry No.—X, 15267-20-6; XI, 15267-21-7; XIII, 15267-22-8; XVIII, 14407-16-0; XXI, 15267-24-0; XXIII, 15267-25-1; XXIV, 15267-26-2; XXV, 15267-27-3; XXVI, 15267-28-4.

(24) A similar experiment with methyl 3-methyl-4-nitro-2-(triphenylphosphoranylidene) butyrate (XII) and *m*-nitrobenzaldehyde yielded methyl *m*-nitrocinnamate.

(25) A similar experiment with methylenetriphenylphosphorane (XIV) and 2-nitro-2-butene gave 1,2-dimethyl-1-nitrocyclopropane (7%, stereochemistry unestablished). The conditions for formation of nitrocyclopropanes from either methylenetriphenylphosphorane (XIV) or ethylidenetriphenylphosphorane were not optimized because of the greater promise of dimethylsulfoxonium methylide (XVIII) as a reagent.

(26) (a) The reaction is exothermic; (b) addition of XVIII to the nitro olefins resulted in extensive polymerization; (c) under usual circumstances there were no (lachrymatory) nitroolefins in the reaction products.

(27) E. Le Goff, *J. Org. Chem.*, **29**, 2048 (1964).

(28) M. S. Silver, M. C. Caserio, H. E. Rice, and J. D. Roberts, *J. Amer. Chem. Soc.*, **83**, 3671 (1961).