4.8 (d, 4, two OH, disappears on exchange with $D_2O$), the latter superimposed on a one-proton multiplet near 4.75 (H-8), 3.3–3.8 (five-proton multiplet), 1.08 (d, 5, C-10 methyl), and 0.74 ppm (C-5 methyl).

*Anal.* Calcd for $C_{15}H_{20}O_5$: C, 64.27; H, 7.19; O, 28.54. Found: C, 64.43; H, 7.23; O, 28.88.

(B) Powdered *H. autumnale* L. (5.4 kg), collected by Mr. Robert R. Lazor at the east end of the bridge on Florida Route 20 over the Apalachicola River near Bristol, Liberty County, Fla., in Sept 1968 (Lazor voucher no. 1306 on deposit in the herbarium at Florida State University), was extracted with chloroform and worked up in the usual way. Chromatography of the crude gum (79 g) over 800 g of silicic acid gave in the benzene eluates a small amount of a triterpene mixture. Benzene–chloroform (2:1 and 1:1) gave mixtures. Elution with chloroform gave 20 g of helenalin. Elution with chloroform–ether (9:1 and 8:2) gave mixtures which were not separated satisfactorily on rechromatography.

Extraction of *H. autumnale* L., collected by Mr. R. Lazor and Dr. R. K. Godfrey on Sept 9, 1968, 13 miles south of Moultrie, Ga. (Lazor–Godfrey voucher no. 1185 on deposit in the herbarium of Florida State University), gave results which did not differ significantly from the ones described in the preceding paragraph.

**Linifolin A.**—Dehydro-2-acetylflexuosin A (**3**) (100 mg) was heated at 180° under nitrogen for 1 hr. The straw-colored solid which formed on cooling was dissolved in benzene and recrystallized to give 95 mg of linifolin A, mp 202–203° (lit. mp 202–204°), mixture melting point with authentic material, undepressed, and nmr and ir spectra superimposable.

**Reaction of Flexuosin A with Thionyl Chloride.**—A solution of 0.15 g of flexuosin A in 3 ml of dry pyridine was mixed with 10 drops of thionyl chloride at 0°, left at room temperature for 4 hr, and then poured on ice. The product was extracted with ether. The ether extract was washed, dried, and evaporated. The amorphous residue which could not be recrystallized satisfactorily exhibited ir bands at 1770 (γ-lactone), 1745, and 1200 $cm^{-1}$ (acetate), but had no bands characteristic of hydroxyl or sulfite functions. The product gave a positive test for chlorine.

**Reactions of 2-Acetylflexuosin.**—Acetylation of 120 mg of 2-acetylflexuosin A with acetic anhydride–pyridine in the usual manner afforded, after recrystallization from ether–petroleum ether, 102 mg of material, mp 130–131°, which was identical in all respects (tlc, mixture melting point, and ir and nmr spectrum) with authentic diacetylflexuosin A.

To a solution of 150 mg at 2-acetylflexuosin A in 6 ml of acetone was added dropwise 0.5 ml of Jones reagent[17] with stirring at 0°. After 20 min at room temperature, excess oxidant was destroyed by adding a few drops of methanol. The solution was diluted with water and extracted with ether. Removal of ether followed by recrystallization from acetone–isopropyl ether afforded 114 mg of dehydro-2-acetylflexuosin A (**3**), which had mp 168–170°; ir 1765 and 1670 (unsaturated lactone), 1750 (cyclopentanone), 1740 (esters), and 1410 $cm^{-1}$ ($CH_2CO$); nmr 6.18 (d, 3.5) and 5.61 (d, 3, $=CH_2$), 5.95 (d, 3.5, H-6), 5.12 (dq, 12, 7, 3, H-2), 4.51 (td 10, 3, H-8), 3.2 (m, three protons, H-3 and H-7), 2.03 and 1.97 (acetates), 1.09 (C-10 methyl), and 1.06 ppm (C-5 methyl); ORD (*c* 0.083, methanol) $[\Phi]_{600}$ 397°, $[\Phi]_{589}$ 442°, $[\Phi]_{310}$ 4575°, $[\Phi]_{276}$ −485°, $[\Phi]_{230}$ 3170°.

*Anal.* Calcd for $C_{19}H_{24}O_7$: C, 62.63; H, 6.60; O, 30.28. Found: C, 62.70; H, 6.67; O, 30.35.

**Diacetylautumnolide.**—A mixture of 100 mg of autumnolide, 1 ml of pyridine, and 1 ml of acetic anhydride was heated at 80° for 2 hr. After the usual work-up the crude product was chromatographed over 2 g of silicic acid. Chloroform eluted a product (single spot on tlc) which was recrystallized from ether: yield 52 mg; mp 101–103°; $[\alpha]^{26}D$ −14.6° (*c* 0.835, $CHCl_3$); nmr 6.24 (d) and 5.71 (d, 2, $=CH_2$), 4.70 (d, 6, H-6), and 4.63 (H-4) superimposed on 4.65 (m, H-8), 3.3 (two protons, H-2 and H-3) superimposed on 3.3 (m, H-7), 2.04 and 2.02 (acetates), 1.18 (d, 6, C-10 methyl), and 1.09 ppm C-5 methyl).

*Anal.* Calcd for $C_{19}H_{24}O_7$: C, 62.63; H, 6.64; O, 30.73. Found: C, 62.48; H, 6.75; O, 30.88.

Attempts to prepose a monoacetyl derivative by acetylation at room temperature resulted in the formation of a glass which appeared to polymerize on standing.

**Oxidation of Autumnolide.**—Oxidation of 50 mg of autumnolide in 3 ml of acetone with 0.2 ml of Jones reagent in the usual manner afforded a colorless solid mixture (tlc). Preparative tlc over silica gel (developer 6% methanolic chloroform) and recrystallization from acetone–ether permitted isolation of 8 mg of the compound responsible for the major spot. It gave a positive 2-epoxy ketone test with potassium iodide and negative ferric chloride and Zimmermann tests. The poorly resolved nmr spectrum exhibited signals at 5.5 (m, H-8), 3.75 (m, two protons, H-2 and H-3), 1.83 (br, C-11 methyl), and 1.30 (d, 6, C-10 methyl).

**Registry No.**—**2c**, 20483-26-5; **3**, 20505-31-1; **7**, 20505-32-2; diacetyl **7**, 20483-27-6.

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[17] L. Fieser and M. Fieser, "Reagents for Organic Synthesis," John Wiley & Sons, Inc., New York, N. Y., 1967, p 142.

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# Cleavage of α-Nitro Ketones

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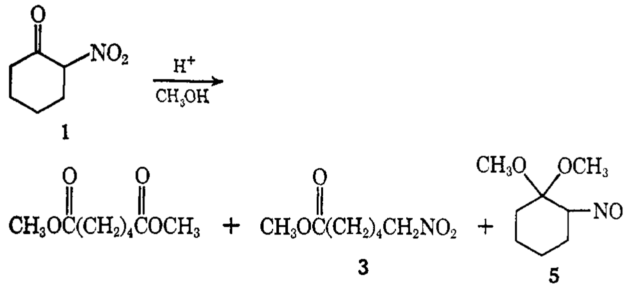
The cleavage of α-nitro ketones has been recently the subject of several investigations.[2-7] In a previous publication we noted that in refluxing methanolic acetic acid 2-nitrocyclohexanone (**1**) and 2-nitro-3,5,5-trimethylcyclopentanone (**2**) were converted into methyl 6-nitrohexanoate (**3**) and methyl 2,2,4-trimethyl-5-nitropentanoate, respectively, while under similar conditions 2-nitrocycloheptanone (**4**) and 2-nitrocyclooctanone failed to react.

In continuation of our work we have found that cleavage in methanol containing a catalytic amount of concentrated sulfuric acid at room temperature led to different products. As shown in Table I, **1** was converted into dimethyl adipate, 2,2-dimethoxynitrocyclohexane (**5**), and **3** (eq 1). Nitro ketone **4** behaved similarly.



(1)

The respective α-nitro ketals were prepared directly from **1** and **4** in high yield by an acid-catalyzed reaction

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[1] Dow Chemical Corp. Fellow, 1963–1964.

[2] H. Feuer and P. M. Pivawer, *J. Org. Chem.*, **31**, 3152 (1966).

[3] A. S. Matlack and D. S. Breslow, *ibid.*, **32**, 1995 (1967).

[4] R. G. Pearson, D. H. Anderson, and L. L. Alt, *J. Amer. Chem. Soc.*, **77**, 527 (1955).

[5] H. O. Larson and E. K. Wat, *ibid.*, **85**, 827 (1963).

[6] A. Hassner and J. Larkin, *ibid.*, **85**, 2181 (1963).

[7] T. Simmons and K. L. Kreuz, *J. Org. Chem.*, **33**, 836 (1968).

Table I

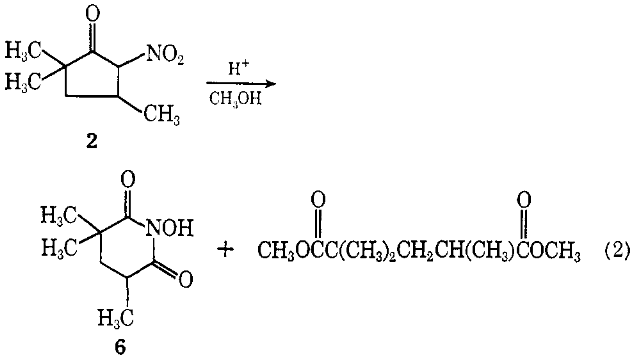
Products of the Acid-Catalyzed Cleavage of α-Nitro Ketones

| α-Nitro ketone | Registry no. | Products (yield, %) |
|---|---|---|
| α-Nitrocyclohexanone[a−c] | 4883-67-4 | Dimethyl adipate (53), methyl 6-nitrohexanoate (3), 2,2-dimethoxynitrocyclohexane (14) |
| α-Nitrocycloheptanone[d,e] | 13154-27-3 | Dimethyl pimelate (28), methyl 7-nitroheptanoate (12), 2,2-dimethoxynitrocycloheptane (4) |
| α-Nitrocycloheptanone[f] | | Diethyl pimelate (65) |
| α-Nitrocyclooctanone[f] | 13154-28-4 | Diethyl suberate (55) |
| 3-Nitro-4-heptanone[f] | 13154-33-1 | Ethyl butyrate, ethyl propionate |
| 3-Nitro-3-methyl-2-butanone[f−i] | 13292-96-1 | Ethyl acetate, 2-nitropropane (12) |
| 2-Bromo-2-nitrocyclooctanone[f] | 20642-74-4 | Diethyl suberate (60), ethyl 8-bromo-8-nitrooctanoate (17) |
| 2-Nitro-1-tetralone[f] | | No reaction |

[a] The reaction was carried out in methanol at room temperature for 3 hr in the presence of catalytic amounts of concentrated sulfuric acid. [b] According to ref 3, in aqueous sodium bicarbonate the product was 6-nitrohexanoic acid. [c] According to ref 7, in concentrated sulfuric acid adipic acid was the product. [d] Reaction condition as in footnote *a* except that the reaction time was 4 hr. [e] 50% of ketone was recovered. [f] The reaction was carried out in absolute ethanol and concentrated sulfuric acid at reflux temperature for 3 hr. [g] 88% of ketone was recovered after a reaction time of 16 hr. [h] The experiment was performed by M. Auerbach. [i] According to ref 7, no reaction occurred in concentrated sulfuric acid.

with methyl orthoformate.[8] Very little ring cleavage occurred during this transformation.

On the other hand, **2** reacted differently from the other nitro ketones, giving rise to N-hydroximide **6** and to a small amount of dimethyl 2,2,4-trimethylglutarate (eq 2).



**2**

**6**

$$CH_3O\overset{O}{\overset{\|}{C}}C(CH_3)_2CH_2CH(CH_3)\overset{O}{\overset{\|}{C}}OCH_3 \quad (2)$$

Both Larson[5] and Hassner[6] reported that this unusual ring expansion with cyclic five-membered-ring α-nitro ketones proceeded in the presence of hydrochloric acid and acetic anhydride. Compound **2** was converted on treatment with hydrochloric acid into **6** (70% yield), but did not react with acetic anhydride.

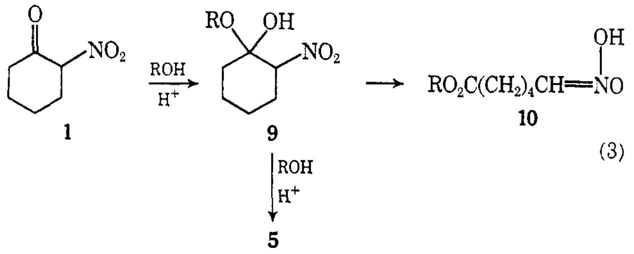
2-Bromo-2-nitro-3,5,5-trimethylcyclopentanone (**7**) and 2-bromo-2-nitrocyclooctanone (**8**) did not react with concentrated hydrochloric acid at 40°. Nevertheless **8** was cleaved readily in refluxing ethanol in the presence of catalytic amounts of sulfuric acid (Table I).

## Discussion

In 1957, Feuer, *et al.*,[9] proposed that cleavage of 2,5-dibromo-2,5-dinitrocyclopentanone which proceeded readily in methanol and dry hydrogen chloride to yield methyl 2-bromo-2-nitroglutarate and methyl 2,5-dibromo-2,5-dinitropentanoate involved formation of a hemiketal. We suggest a similar mechanism to explain the cleavage of α-nitro ketones (eq 3). The important step in this mechanism is the formation of hemiketal **9** with subsequent cleavage to an *aci*-nitro intermediate **10**. Formation of **9** during the reaction was clearly indicated by the fact that α-nitro ketals were isolated from the acidic cleavage of **1** and **4**. Intermediate **10** is preferentially converted into an ω-nitrocarboxylic ester (or acid) in weakly acidic[2] or basic[3] media, and to a dicarboxylic ester (or acid), possibly *via* a modified Nef reaction,[10] in strongly acid solutions.

As suggested by Simmons and Kreuz,[7] the conversion of α-nitro ketones into carboxylic acids in strong acidic media could involve the direct conversion of a protonated form of **1** into a nitrile oxide, but this reaction path does not explain the ready cleavage of compounds **7**, **8**, and 3-nitro-3-methyl-2-butanone (**11**) containing *t*-nitro groups. In fact, it was reported that **11** did not undergo cleavage when treated with excess 96% sulfuric acid.[7] On the other hand, the formation of hemiketals as intermediates explains the facile cleavage of α-nitro ketones in alcohol in the presence of catalytic amounts of acid.

A possible explanation for the failure of α-nitrotetralone (**12**) to cleave in the acid-catalyzed reaction with methanol might be its failure to form a hemiketal. This could also account for our observation that **12** did not give a ketal on treatment with methyl orthoformate. It is of interest that Pearson[4] observed that ω-nitroacetophenone did not cleave in aqueous hydrochloric acid.



**1** **9** **10** **5**

## Experimental Section

Gas chromatographic analysis was performed on an Aerograph A903 at 135° using a 4-ft SF-96 on Chromosorb column.

**Reaction of α-Nitro Ketones in Refluxing Absolute Ethanol.**— The following experiment is typical of the procedure employed. 2-Nitrocycloheptanone (**4**, 2.0 g, 0.012 mol) and 3 drops of concentrated sulfuric acid were added to 25 ml of absolute ethanol and the reaction mixture was refluxed until **4** could no longer be detected by glpc (3 hr). Sodium acetate was added to neutralize the acid followed by 100 ml of ether to precipitate inorganic salts. After filtration and evaporation of solvents, the residue was distilled to give 1.8 g (65%) of diethyl pimelate, bp 65–66° (0.05 mm), $n^{20}D$ 1.4301 (lit.[11] $n^{20}D$ 1.4299).

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(8) L. Claisen, *Chem. Ber.*, **29**, 1007 (1896).

(9) H. Feuer, J. W. Shepherd, and C. Savides, *J. Amer. Chem. Soc.*, **79**, 5768 (1957).

(10) W. E. Noland, *Chem. Rev.*, **55**, 137 (1955).

**Reaction of 2-Nitro Ketones in Methanol at Room Temperature. A. 2-Nitrocycloheptanone (4).**—Compound **4** (0.8 g, 0.005 mol) and 5 drops of concentrated sulfuric acid were added to 50 ml of absolute methanol and the mixture was allowed to stir for 20 hr. After neutralization with sodium acetate, 200 ml of ether was added to precipitate inorganic salts. The reaction mixture was filtered and the solvent evaporated. Distillation of the residue gave 0.9 g of material, bp 60–80° (0.2 mm). Glpc analysis revealed four components: **4** (50%), dimethyl pimelate (28%), methyl 7-nitroheptanoate (12%), and 2,2-dimethoxynitrocycloheptane (4%). The retention times of these compounds were identical with those of authentic samples.

**B. 2-Nitro-3,5,5-trimethylcyclopentanone (2).**—Compound **2** (1.5 g, 0.0088 mol) was added to 25 ml of absolute methanol followed by 5 drops of concentrated sulfuric acid. After being stirred for 96 hr the reaction mixture was worked up in the manner as described in experiment A. Distillation gave 0.8 g of material, bp 45–62° (0.5 mm), and 0.5 g of a high boiling material which solidified in the distilling head.

Glpc analysis of the fraction, bp 45–62°, revealed two components, unreacted **2** (46%) and dimethyl 2,2,4-trimethylglutarate (5%). The ester was purified by glpc: $n^{20}\text{D}$ 1.4305 (lit.[12] $n^{21.5}\text{D}$ 1.4309).

Recrystallizing the high boiling material from *n*-heptane gave 0.4 g (33%) of 2,6-dioxo-3,3,5-trimethyl-1-hydroxy-1-azacyclohexane (**6**): mp 118–119.5°; ir (Nujol) 3350 (OH) and 1740 and 1665 cm$^{-1}$ (C═O); nmr ($CDCl_3$) δ 1.32 [t, 9, $C(CH_3)_2$ and $C(CH_3)$], 1.69 (d, 1, $J$ = 3 Hz, H, equatorial in $CH_2$), 1.83 (s, 1, H axial in $CH_2$), 2.80 (m, 1, CH), and 7.60 (s, 1, OH).

*Anal.* Calcd for $C_8H_{13}NO_3$: C, 56.14; H, 7.60; N, 8.18. Found: C, 56.35; H, 7.68; N, 8.19.

When the reaction was carried out in refluxing methanol for 20 hr, 1.0 g of **2** yielded 0.7 g (58%) of diester and 0.25 g (25%) of **6**.

When 0.5 g of **2** was allowed to stir at room temperature for 12 hr in 10 ml of concentrated hydrochloric acid, 0.35 g (70%) of **6**, mp 118–119°, was obtained after evaporation of the aqueous solution and sublimation of the residue at 40° (0.05 mm).

**Acetate of 6.**—To 10 ml of acetic anhydride was added 0.1 g of **6** and, after the mixture stirred for 24 hr, excess acetic anhydride was removed *in vacuo*. The residue, 0.11 g (100%) was purified by glpc: $n^{20}\text{D}$ 1.4680.

*Anal.* Calcd for $C_{10}H_{15}NO_4$: C, 56.34; H, 7.04; N, 6.57. Found: C, 56.44; H, 7.08; N, 6.33.

**2,2-Dimethoxynitrocycloheptane.**—To a mixture of 10 g of absolute methanol, 7.0 g of methyl orthoformate, and 3 drops of concentrated sulfuric acid was added 1.0 g (0.0062 mol) of **4**. After 12 hr at room temperature sodium bicarbonate was added to neutralize the acid, the reaction mixture filtered, and the solvent was evaporated. Distillation gave 1.2 g of material, bp 55–62° (0.4 mm). Glpc analysis revealed the presence of three components: **4** (10%), dimethyl pimelate (18%), and 2,2-dimethoxynitrocycloheptane (72%). Dimethyl pimelate and **4** were identified by comparison of their retention times with those of authentic samples. 2,2-Dimethoxynitrocycloheptane was purified by glpc: $n^{20}\text{D}$ 1.4760; ir (neat) 1550 and 1370 ($NO_2$) and 1110 cm$^{-1}$ ($OCH_3$).

*Anal.* Calcd for $C_9H_{17}NO_4$: C, 53.20; H, 8.37; N, 6.90. Found: C, 53.34; H, 8.21; N, 6.83.

Similarly was prepared **2,2-dimethoxynitrocyclohexane** (83%), mp 53–54° after recrystallization from methanol.

*Anal.* Calcd for $C_8H_{15}NO_4$: C, 50.79; H, 7.94; N, 7.41. Found: C, 50.74; H, 8.08; N, 7.20.

**2-Bromo-2-nitro-3,5,5-trimethylcyclopentanone (7).**—Potassium 2-keto-3,3,5-trimethylcyclopentanenitronate[2] (2.1 g 0.01 mol) was placed in 25 ml of carbon tetrachloride and bromine was added until a faint yellow color persisted. The mixture was filtered and the filtrate was evaporated. The residual solid was recrystallized from hexane to give 2.0 g (67%) of compound **7**: mp 49–51°; ir (melt) 1515 and 1350 ($NO_2$) and 1755 cm$^{-1}$ (C═O).

*Anal.* Calcd for $C_8H_{12}BrNO_3$: C, 38.40; H, 4.80; N, 5.60; Br. 32.00. Found: C, 38.44; H, 4.91; N, 5.63; Br, 32.40.

**Registry No.**—2,2-Dimethoxynitrocycloheptane, 20642-76-6; 2,2-dimethoxynitrocyclohexane, 20642-78-8; **6**, 20642-75-5; **7**, 20642-77-7.

**Acknowledgment.**—We are indebted to the Office of Naval Research for the financial support of this work.

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[11] E. Huntress and S. Mulliken, "Identification of Pure Organic Compounds," John Wiley & Sons, Inc., New York, N. Y., 1941, Order I.

[12] G. R. Enser and W. Wilson, *J. Chem. Soc.*, 4068 (1956).

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# Carbonium-Ion Behavior in Aluminum Bromide–1,2,4-Trichlorobenzene

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Nmr spectroscopy was used to monitor the catalytic activity of the aluminum bromide–1,2,4-trichlorobenzene system and to study long-chain hydride-transfer reactions between paraffins and cations. Compounds containing tertiary C–H bonds generally participate in extremely rapid reactions converting all the paraffins into ions in moments. Rearrangement of the intermediates to ions with a different number of branches is slower and usually rate determining. Ionic rearrangements leading to similarly branched species, however, are fast and these studies do not distinguish between these rates and those of hydride transfer. Normal paraffins appear to react much more slowly, probably because both the rates of forming and rearranging secondary ions are slow.

Aluminum bromide has a long history as an exceedingly active Friedel–Crafts catalyst. It is able to support the formation of alkyl cations which undergo extensive intramolecular isomerization and intermolecular reactions. The intermolecular reactions are generally of two types depending on the presence of unsaturated reactants in the system. When olefinic compounds are present, polymerization usually predominates, although cracking of high molecular weight ions and hydride abstraction reactions from the olefin also are often observed.

In the absence of olefins or other bases the alkyl ions enter into hydride abstraction reactions with paraffins.[1] This reaction is often considered the rate-determining step in the isomerization of paraffins, particularly when a normal paraffin is the hydride donor. Alkyl cations formed over $AlBr_3$ are known to be efficient at abstracting either tertiary or secondary hydride ions and thus participating in long-chain isomerization processes.

A major result of earlier work with this system was the finding that nmr spectroscopy could be used to study long-chain intermolecular hydride-transfer processes between isobutane and low concentrations of *t*-butyl cations,[2] eq 1. It can be shown that the doublet of

$$i\text{-}C_4H_{10} + t\text{-}C_4H_9^+ \rightleftharpoons t\text{-}C_4H_9^+ + i\text{-}C_4H_{10} \qquad (1)$$

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[1] P. D. Bartlett, F. E. Condon, and A. Schneider, *J. Amer. Chem. Soc.*, **66**, 1531 (1944).

[2] G. M. Kramer, B. E. Hudson, and M. T. Melchior, *J. Phys. Chem.*, **71**, 1525 (1967).