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Catalytic Diacetoxylation of Dihaloethylenes in the Presence of Palladium Salts

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The reaction of dihaloethylenes with acetate anions in the presence of palladium(II) salts gave *trans*-diacetoxyethylenes catalytically. It was found that the system, $PdCl_2$–NaOAc–CH_3CN is the best for the diacetoxylation of dihaloethylenes, and that palladium(II) salts catalyze the isomerization of *trans*-diacetoxyethylene to its 1,1-diacetoxy derivative. The mechanism was also discussed.

Palladium salts have been known to cause a wide variety of reaction.[1] It was generally thought that halide ion displacement of vinyl halides with nucleophiles was difficult because of their double bond character between carbon and halogen atoms.

Since Stern *et al.* explored the possibility of the nucleophilic substitution of vinyl chloride by an acetate anion in the presence of palladium(II) chloride to give vinyl acetate,[2] a few reports appeared concerning with the substitution.[3] However, examples are limited to only monohalides such as vinyl chloride or 2-chloropropylene. Interest in whether dihalides also undergo substitution reaction or not, prompted us to investigate the reaction of dihaloethylenes in detail. Interestingly enough we have found that in the presence of catalytic amounts of palladium(II) salts, various dihaloethylenes such as dichloro-, dibromo-, diiodo-, and bromochloroethylenes react readily with an acetate anion to produce diacetoxyethylenes,[4] and that they also react with various substituted acetate anions (XCH_2COO^-: X= C_2H_5, CH_3, Cl). In addition, in the course of this study, an isomerization of *trans*-diacetoxyethylene to 1,1-diacetate by palladium(II) salts was also found.

In this paper, we will describe the substitution reaction of dihaloethylenes with acetate anions, and the observation that *trans*-diacetoxyethylene isomerizes to its 1,1-diacetate derivatives in the presence of palladium(II) salts.

Results and Discussion

Reaction of cis-*Dichloroethylene with Acetate Anion.* In the substitution reaction of vinyl halide, the system, $PdCl_2$–Na_2HPO_4–isooctane-acetic acid was used,[2] but a dihaloethylene, *cis*-dichloroethylene, afforded no acetates under the similar reaction conditions. So, first, we investigated the reaction conditions under which the olefinic dihalides suffer the nucleophilic substitution reaction with an acetate anion.

Table 1. Diacetoxylation of *cis*-dichloroethylene by palladium(II) salts[a)]

Palladium salt	Acetoxylating agent	Solvent	Yield, %[b)] of *trans*-diacetoxyethylene
$Pd(OAc)_2$	AcOH	Isooctane	trace
$Pd(OAc)_2$	AcOH	—	trace
$Pd(OAc)_2$	—	Acetonitrile	7[c)]
$PdCl_2$	NaOAc	Acetic acid	14[c)]
$PdCl_2$	NaOAc	Acetonitrile	123[c)]
$PdCl_2$	NaOAc	Dimethylformamide	42[c)]
$PdCl_2$	NaOAc	Benzonitrile	8[c)]
$PdCl_2$	NaOAc	Ethanol	trace
$PdCl_2$	NaOAc	Pyridine	—
$PdCl_2$[d)]	AcOH	Isooctane	—

a) Reactions were carried out at 80°C for 8 hr unless otherwise stated.

b) Based on the Pd(II) catalyst.

c) 1,1-Diacetoxyethylene and *cis*-isomer were also formed in small amount.

d) Disodium hydrogen phosphate (Na_2HPO_4) was employed and the reaction was performed for 48 hr at room temperature.

Table 1 summarizes the results and shows that the system, $PdCl_2$–NaOAc can cause the diacetoxylation of *cis*-dichloroethylene catalytically, and that acetonitrile is the best solvent for the reaction. It seems that the solvent which has an appropriate ability of coordination to palladium(II) and can be easily displaced by the substrate dihalo-olefin, is suitable for the reaction. In typical, the reaction of *cis*-dichloroethylene with sodium acetate in the presence of a catalytic amount of $PdCl_2$ gave *trans*-diacetoxyethylene (123%[5)]) and 1,1-diacetoxyethylene (39%) with a small amount of

Table 2. Reactivity of palladium(II) salts[a)]

Palladium salt	Product and yield, %[b)]	
	trans-diacetoxy-	1,1-diacetoxyethylene
$PdCl_2$	123	39[c)]
$PdBr_2$	36	9
PdI_2	0.5	trace

a) Reactions were carried out at 80°C for 8 hr charging 0.09 mol of *cis*-dichloroethylene, 0.18 mol of NaOAc, 0.03 mol of palladium salt, and 200 m*l* of CH_3CN as a solvent.

b) Yields are based on palladium salt used.

c) *cis*-Isomer was also formed in a very small amount.

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[1] For example, P. M. Maitlis, "The Organic Chemistry of Palladium," Vol. I and II, Academic Press, New York, 1971.

[2] E. W. Stern, M. L. Spector, and H. P. Lefti, *J. Catal.*, **6**, 152 (1966).

[3] a) C. F. Kohll and R. van Helden, *Rec. Trav. Chim. Pays-Bas*, **87**, 481 (1968); b) H. C. Volger, *ibid.*, **87**, 501 (1968); c) M. Tamura and A. Yasui, *Kogyo Kagaku Zasshi*, **72**, 572 (1969); d) P. M. Henry, *J. Amer. Chem. Soc.*, **93**, 3853 (1971); **94**, 1527 (1972).

[4] M. Yamaji, Y. Fujiwara, T. Imanaka, and S. Teranishi, This Bulletin, **43**, 2659 (1970).

[5] Yields given in this paper are based on the amount of palladium salt used.

cis-diacetoxyethylene. And interestingly in this case, no monoacetate was produced.

In order to study the ligand effect on the reaction, the reactivities of $PdCl_2$, $PdBr_2$, and PdI_2 were compared (Table 2). The reactivity decreases in the order: Cl>Br>I. This may be explained in the following way: π-acceptor character increases with the order, Cl<Br<I,[6] so back donation from palladium to the substrate dihalo-olefin would be more restricted in the case of PdI_2. Thus the ease with which palladium(II) and the olefin form a stable π-complex, increases in the order, I<Br<Cl, then resulting in increase of the reactivity in this order. In addition, the bulkiness of the iodine atom would prevent the coordination of the substrate olefin to palladium(II). Consequently, $PdCl_2$–NaOAc–CH_3CN is the most effective system for the diacetoxylation of dihaloethylene.

The acetoxylation of *cis*-dichloroethylene gave 1,1- and *cis*-diacetoxyethylene as by-products. In order to study the reaction path of these products, isomerization of *trans*-diacetoxyethylene, a main product, was examined (Table 3).

TABLE 3. ISOMERIZATION OF *trans*-DIACETOXYETHYLENE[a)]

$PdCl_2$ mmol	NaOAc mmol	Reaction time, hr	Yield, %[b)] diacetoxyethylenes	
			1,1-isomer	*cis*-isomer
0.06	None	6	31	trace
0.06	0.12	8	64	trace
None	0.12	8	—	30
0.06[c)]	0.12	8	trace	98

a) Reactions were carried out at 80°C for 8 hr using CH_3CN as a solvent.
b) Based on *trans*-diacetoxyethylene.
c) The starting material was *cis*-diacetoxyethylene.

As is apparent from Table 3, *trans*-diacetoxyethylene isomerized to 1,1-diacetate (64% yield) in the presence of $PdCl_2$ and NaOAc. In addition, the table indicates that thermal isomerization of *trans*-diacetoxyethylene to its *cis* isomer takes place in the absence of $PdCl_2$. Therefore, it seems that both 1,1-diacetoxyethylene and its *cis* isomer[7)] are derived from *trans*-diacetoxyethylene which is formed by diacetoxylation of the starting *cis*-dichloroethylene.

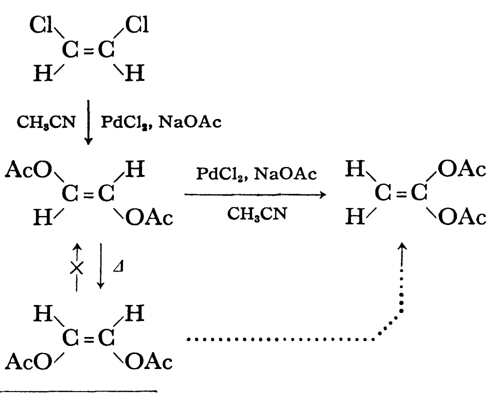

TABLE 4. REACTION OF *cis*-DICHLOROETHYLENE WITH SUBSTITUTED ACETATE ANIONS[a)]

Sodium salt	Yield, % of diacetate[b)]	
	trans-isomer	1,1-isomer
C_2H_5–CH_2COONa	77	14[c)]
CH_3–CH_2COONa	55	11[d)]
Cl–CH_2COONa	trace[e)]	—

a) Reactions were all carried out at 80°C for 8 hr, charging 0.02 mol of $PdCl_2$, 0.12 mol of sodium salt, 0.06 mol of *cis*-dichloroethylene, and 160 ml of CH_3CN.
b) Based on $PdCl_2$ used.
c) A trace amount of butyric anhydride was also formed.
d) A trace amount of propionic anhydride was also formed.
e) 1-Chloro-2-chloroacetoxyethylene was formed in a 0.4% yield.

Reaction of cis-*Dichloroethylene with Substituted Acetate Anions.* As it became apparent that $PdCl_2$–NaOAc causes diacetoxylation of *cis*-dichloroethylene, we further tried to extend this reaction. Examination was performed using the substituted acetate anions (XCH_2-COO^-: X=C_2H_5, CH_3, Cl) as nucleophiles. The data listed in Table 4 show that the diacetoxylation could also occur in the cases of sodium butyrate, propionate, and chloroacetate other than sodium acetate, and that an electron donating group (CH_3, C_2H_5) increases the reactivity, indicating the nucleophilic nature of the reaction.

Reaction of trans-*Dichloroethylene, -Diiodoethylene, -Bromoiodoethylene, and-Dibromoethylene with Acetate Anion.* Since *cis*-dichloroethylene has been found to undergo diacetoxylation, other dihaloethylenes were investigated toward the reactivity in the presence of $PdCl_2$ and NaOAc (Table 5).

TABLE 5. DIACETOXYLATION OF VARIOUS DIHALOETHYLENES[a)]

Dihaloethylene	Yield, % of diacetoxyethylene[b)]			
	trans-	1,1-	*cis*-	Total
trans-ClHC=CHCl	138	70	trace	208
cis-ClHC=CHCl	123	39	trace	162
BrHC=CHBr[c)]	160	30	trace	190
trans-BrHC=CHI	33	23	5	61
trans-ICH=CHI	3	2	—	5

a) Reactions were carried out at 80°C for 8 hr using CH_3CN as a solvent.
b) Based on $PdCl_2$.
c) *cis* and *trans* Mixture (5:7).

It can be seen from Table 5, various dichloroethylenes can undergo diacetoxylation in the presence of $PdCl_2$ and NaOAc as *cis*-dichloroethylene does. The reactivity decreases in the order: Cl>Br>I.

1,2-Transfer of Acetoxy Group on Ethylenic Carbon Atoms. As mentioned above, it has been found that $PdCl_2$ catalyzes the isomerization of *trans*-diacetoxyethylene to 1,1-diacetoxyethylene. Palladium chloride without NaOAc can also affect the isomerization, but the yield decreases from 64% to 31%. This indicates that an acetate anion of NaOAc other than the starting *trans*-

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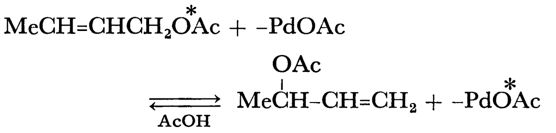
[6)] J. Chatt and B. L. Shaw, *J. Chem. Soc.*, **1962**, 5075.

[7)] *cis*-Diacetate produced in a small amount is not an initial product since it does not isomerize to *trans*-diacetate under the reaction conditions.

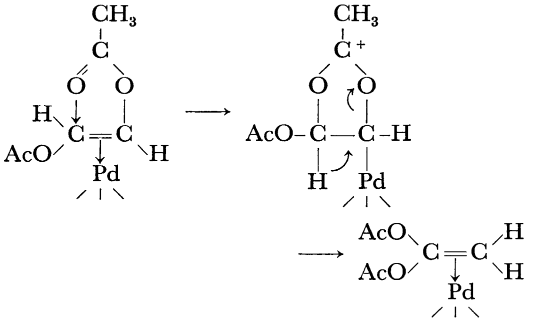
diacetoxyethylene, is partly involved in the reaction.[8]

Palladium(II) catalyzed allylic isomerization of an acetate anion is well known,[9] but vinylic isomerization is the first example to our knowledge. Henry reported a palladium(II) catalyzed allylic isomerization of an acetate anion, and that two reactions actually take place involving an acetoxypalladation-deacetoxypalladation mechanism and 1,3-acetoxonium ion mechanism.[9]

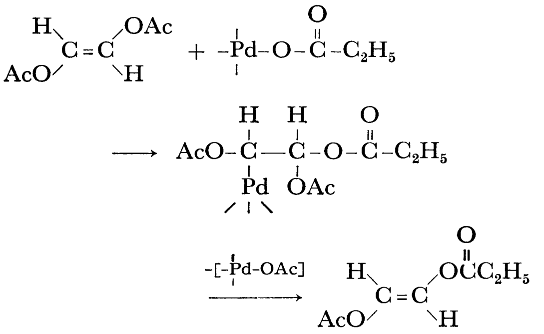


$$\mathrm{MeCH{=}CHCH_2\overset{*}{O}Ac + {-}PdOAc \underset{AcOH}{\rightleftarrows} Me\overset{OAc}{C}H{-}CH{=}CH_2 + {-}Pd\overset{*}{O}Ac} \quad (1)$$

In the present case, the isomerization reaction might proceed through a 1,2-acetoxonium intermediate (Eq. 2), and an acetoxypalladation-deacetoxypalladation might be operative in the exchange reaction of acetate anions (Eq. 3).



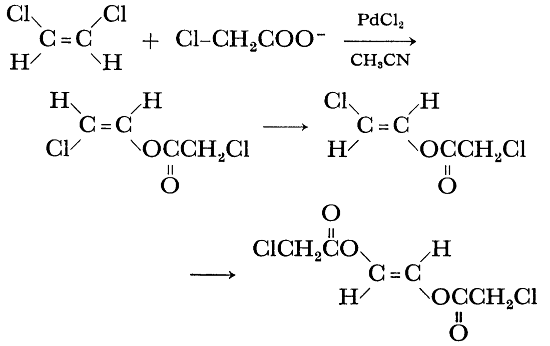
(2)



(3)

$PdBr_2$, PdI_2, $Pd(OAc)_2$, and $PdCl_2(CH_3CN)_2$ gave the isomerization but other metal salts, such as $RhCl_3$, $IrCl_3$, $NiCl_2$, $PtCl_2$, $FeCl_3$, or $CoCl_2$ gave no reaction.[10] Thus it can be said that this isomerization is characteristic for Pd(II) salts. This provides a very convenient synthetic method for preparing 1,1-diacetoxyethylene of which preparation was rather troublesome by other methods.

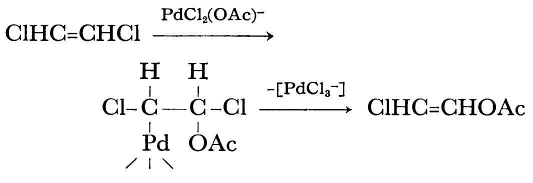
Mechanism of Acetoxylation. The Pd(II) catalyzed acetoxylation of dihaloethylenes gives a *trans*-diacetate as a main product. It seems that the acetoxylation takes place step by step[11] since the monoacetate was obtained from the reaction of *cis*-dichloroethylene and sodium chloroacetate.



(4)

Finally, the diacetoxylation would proceed through the similar mechanism proposed to the acetoxylation of vinyl halides.[1,3a)]

$$\mathrm{PdCl_2 + AcO^- \rightleftarrows PdCl_2(OAc)^-} \quad (5)$$

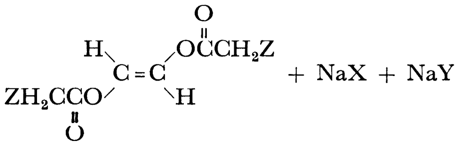


$$\mathrm{ClHC{=}CHCl \xrightarrow{PdCl_2(OAc)^-} Cl{-}\underset{Pd}{\overset{H}{C}}{-}\underset{OAc}{\overset{H}{C}}{-}Cl \xrightarrow{-[PdCl_3^-]} ClHC{=}CHOAc} \quad (6)$$

$$\mathrm{ClHC{=}CHOAc \xrightarrow{PdCl_2(OAc)^-} AcOHC{=}CHOAc + PdCl_2 + Cl^-} \quad (7)$$

In conclusion, olefinic dihalides such as dihaloethylenes can also undergo acetoxylation by palladium(II) salt catalysts, to give *trans*-diacetates rather exclusively (Eq. 8). In addition, palladium(II) salts affect the isomerization of *trans*-diacetates to their 1,1-diacetate derivatives. These reactions provide a very convenient route to a wide variety of diacetate derivatives.

$$\mathrm{XHC{=}CHY + 2ZCH_2COONa \xrightarrow[CH_3CN]{PdCl_2}}$$



(8)

Experimental

All temperatures were uncorrected. The IR spectra were recorded on a JASCO IR-E spectrometer and the NMR spectra were measured on a Japan Electron Optics JNM-4H-100 spectrometer. Chemical shifts are given in τ units together with splitting patterns and relative integrated area.

Materials. *cis*- and *trans*-Dichloroethylene, and dibromoethylene (5: 7 *cis* and *trans* mixture) were commercial grade and distilled before use. *trans*-Diiodoethylene (mp 73—73.5°C)[12] and *trans*-bromoiodoethylene (bp 70—71°C/40-mmHg)[13] were prepared according to the methods reported.

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[8] This external acetate anion participation was confirmed by the fact that dipropionyloxyethylenes were obtained when *trans*-diacetoxyethylene was treated with sodium propionate and palladium chloride.[3d)]

[9] P. M. Henry, *Chem. Commun.*, **1971**, 328.

[10] In the case of allylic isomerization, $PdCl_2$, $PtCl_2$, $RuCl_3$, $OsCl_3$, and $RhCl_3$ are reported to be effective catalysts.[9]

[11] The reaction of the monoacetate to the diacetate may be very fast since no monoacetate was obtained in the reaction of dihaloethylenes with an acetate anion, and the *cis-trans* isomerization might take place in the stage of the monoacetate presumably due to its thermal stability.

[12] A. Sabanejeff, *Ann. Chem.*, **178**, 109 (1875).

[13] H. G. Viehe and E. Franchimont, *Ber.*, **96**, 3153 (1963).

Palladium(II) salts were commercial grade.

General Procedure for Diacetoxylation of Dihaloethylenes with Acetate Anion. Mixtures of the palladium salt, the dihaloethylene in three equiv amount, sodium acetate in six equiv amount, and the solvent were stirred for 8 hr at 80°C. The resulting mixture was filtered to remove $PdCl_2$ and small amounts of Pd metal formed. The filtate was poured into water and the organic material was treated with aqueous sodium carbonate solution, washed with water, and then dried over anhydrous $MgSO_4$. After evaporation of about half of the solvent, the residue was kept standing for several hours, and then *trans*-diacetoxyethylene crystallized, and mother liquid was subjected to preparative gas chromatography (Yanagimoto G-8, Apiezon L) to give 1,1-diacetate and/or *cis* diacetate. Specific examples of the reaction are given in detail below.

Reaction of cis-Dichloroethylene with Sodium Acetate. In a 250 ml, three necked, round-bottomed flask provided with a condenser with a calcium chloride tube at the top, and a stirrer, was placed a mixture of 0.09 mol of *cis*-dichloroethylene, 0.18 mol of sodium acetate, 0.03 mol of $PdCl_2$ and 200 ml of acetonitrile. The mixture was stirred for 8 hr at 80°C. After work-up as decsribed above, the residue crystallized partly. Recrystallization from ether-petroleum ether gave colorless crystals, mp 42—43.7°C. Purification was done by sublimation (4 mmHg) (5.31 g, 123% based on $PdCl_2$), mp 44—45°C which was assigned as *trans*-diacetoxyethylene by comparison of the IR spectra and mixture melting point with an authentic sample,[14] IR (neat) cm^{-1}: 976 (*trans* C-H), 1200 (C–O–C), 1380 (CH_3COO) and 1770 (C=O); NMR (CCl_4): 3.17 (s, 2H) and 7.83 (s, 6H). Found: C, 49.93; H, 5.60%. Calcd for $C_6H_8O_4$: C, 50.00; H, 5.60%.

From the mother liquor, two products were detected and these were separated by glpc. One (1.68 g, 39%) was assigned as 1,1-diacetoxyethylene and the other (trace amount) as *cis*-diacetoxyethylene by comparison with authentic samples,[14] 1,1-diacetoxyethylene; IR (neat) cm^{-1}: 877 (CH_2=), 1200 (C–O–C), 1380 (CH_3COO) and 1760 (C=O); NMR (CCl_4): 2.50 (s, 2H) and 7.80 (s, 6H). *cis*-Diacetoxyethylene; IR (neat) cm^{-1}: 1200 (C–O–C), 1380 (CH_3COO), 1620 (C=C) and 1760 (C=O); NMR (CCl_4): 5.40 (s, 2H) and 7.84 (s, 6H).

From the solvent evaporated, the starting *cis*-dichloroethylene was recovered without isomerization. Authentic *trans*- and *cis*-diacetoxyethylenes and 1,1-diacetate isomer were prepared by the modification of the method described by Shostakovskii *et al.*[14]

Reaction of cis-*Dichloroethylene with Sodium Propionate, Butyrate, and Chloroacetate.* The reaction of *cis*-dichloroethylene with sodium propionate was performed as described above. The products were *trans*-dipropionyloxyethylene (55%), 1,1-dipropionyloxyethylene (11%) and propionic anhydride (trace), *trans*-dipropionyloxyethylene; IR (neat) cm^{-1}: 935, 1150, 1343, 1460, and 1760; NMR (CCl_4): 3.27 (s, 2H), 7.56 (q, 4H, J=7 Hz), and 8.80 (t, 6H, J=7 Hz). 1,1-Dipropionyloxyethylene; IR (neat) cm^{-1}: 900, 1150, and 1750; NMR (CCl_4): 2.26 (s, 2H), 7.64 (q, 4H, J=7 Hz), and 8.84 (t, 6H, J=7 Hz).

Similarly the reaction with sodium butyrate gave *trans*-dibutyryloxyethylene (77%), IR (neat) cm^{-1}: 970, 1245, 1345, and 1760; NMR (CCl_4): 3.27 (s, 2H), 7.62 (t, 4H, J=7 Hz), 8.30 (m, 4H), and 9.00 (t, 6H, J=7 Hz), and 1,1-dibutyryloxyethylene (14%), IR (neat) cm^{-1}: 900, 1150, and 1750; NMR (CCl_4): 2.60 (s, 2H), 7.68 (t, 4H, J=6 Hz), 8.33 (m, 4H), and 9.02 (t, 6H, J=6 Hz), and butyric anhydride (trace).

The reaction with sodium monochloroacetate gave small amounts of 1,2-dichloroacetoxyethylene (probably *trans*), NMR (CCl_4): 3.60 (s, 2H) and 5.98 (s, 4H), and 1-chloro-2-chloroacetoxyethylene (0.4%), NMR (CCl_4): 2.58 (d, 1H, J=4.5 Hz), 4.40 (d, 1H, J=4.5 Hz), and 5.87 (s, 2H).

Isomerization of trans-*Diacetoxyethylene.* The reaction were carried out at 80°C for 8 hr with stirring, charging 0.18 mmol *trans*-diacetoxyethylene, 0.06 mmol of palladium chloride, 0.12 mmol of sodium acetate and 2 ml of acetonitrile. The reaction mixture was analyzed by glcg using tetralin as an internal standard. The results are shown in Table 3.

Isomerization of trans-*Diacetoxyethylene in the Presence of Sodium Propionate.* The reaction was performed at 80°C for 6 hr, charging 0.12 mmol of *trans*-diacetoxyethylene, 0.06 mmol of sodium propionate, 0.056 mmol of palladium chloride and 2.5 m*l* of acetonitrile. After work-up as usual, the reaction mixture was analyzed by glcg. There were obtained *trans*-1-acetoxy-2-propionyloxyethylene (28%), 1,1-diacetoxyethylene (14%) with small amounts of unidentified acetates. The starting *trans*-diacetoxyethylene was recovered in 42% yield. *trans*-1-Acetoxy-2-propionyloxyethylene, IR (neat) cm^{-1}: 945, 1105, 1150, and 1762; NMR (CCl_4): 3.22 (s, 2H), 7.55 (q, 2H, J=7 Hz), 7.80 (s, 3H) and 8.78 (t, 3H, J=7 Hz).

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[14] M. F. Shostakovskii, N. V. Kuznetsov, and Chemin Yang, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1962**, 710.