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3,3-DISUBSTITUTED OXETANES

3,3-BIS(NITROMETHYL)OXETANE AND THE ULTRAVIOLET SPECTRA OF ITS NITRONATE ANIONS

A. T. Nielsen and W. G. Finnegan
Organic Chemistry Branch, Chemistry Division, U.S. Naval Ordnance Test Station,
China Lake, California

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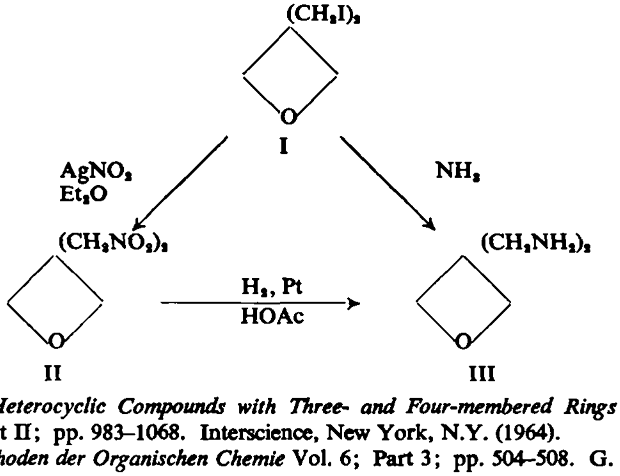
Abstract—3,3-Bis(nitromethyl)oxetane (II) has been prepared by the Victor Meyer reaction from 3,3-bis(iodomethyl)oxetane. The UV spectra of its mono and bisnitronate anions and those of other α,ω-dinitroalkanes formed in 85% ethanolic NaOHaq have been determined and are discussed. The rather high value of the absorption maximum (257 mμ) observed for the bisnitronate anion of II is attributed to the combined electron withdrawing effects of the oxetane ring and the β-carbonitronate group. The results are compared with other data dealing with the effect of small rings on electronic spectra.

Only one C-nitro derivative of oxetane appears to have been described previously.[1–3] 3-Chloromethyl-3-nitroöxetane has been reported as a product of reaction of tris(methylol)nitromethane with phosphorous pentachloride ($<1\%$ yield).[3] No conclusive evidence in support of its structure was provided. An O-nitro derivative, the nitrate ester 3,3-bis(nitratomethyl)oxetane, has been prepared from pentaerythritol trinitrate.[4] The present work describes the first authenticated C-nitro compound incorporating an oxetane ring—3,3-bis(nitromethyl)oxetane. The UV spectra of its mono- and bisnitronate anions have been examined and are discussed relative to the effects of other small rings on electronic spectra.

3,3-Bis(nitromethyl)oxetane (II) has been obtained in 3% yield by reaction of the corresponding iodomethyl compound (I) with silver nitrite in refluxing ether. Its structure was clearly established by hydrogenation (platinum, acetic acid) to 3,3-bis(aminomethyl)oxetane (III), isolated as its known dipicrate derivatives.[5] The diamine



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[1] S. Searles, Jr., *Heterocyclic Compounds with Three- and Four-membered Rings* (Edited by A. Weissberger), Part II; pp. 983–1068. Interscience, New York, N.Y. (1964).

[2] G. Dittus in *Methoden der Organischen Chemie* Vol. 6; Part 3; pp. 504–508. G. Thieme Verlag, Stuttgart (1965).

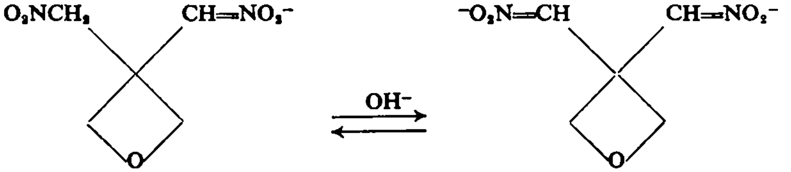
[3] H. Kleinfeller, *Ber. Dtsch. Chem. Ges.* **62**, 1582 (1929).

[4] D. E. Elrick, W. H. Gardner, N. S. Marans and R. F. Preckel, *J. Amer. Chem. Soc.* **76**, 1374 (1954).

[5] M. Beyaert and F. Govaert, *Proc. Acad. Sci. Amsterdam* **42**, 776 (1939); *Chem. Abstr.* **34**, 5414 (1940).

was also prepared by reaction of I with aqueous ethanolic ammonia. As noted with other dinitroalkanes,[6] hydrogenation of II occurred quite rapidly during absorption of four mole-equivalents of hydrogen, followed by very slow absorption of the remaining two mole-equivalents. This result argues for intervention of the intermediate, 3,3-bis(hydroxylaminomethyl)oxetane, by analogy with previous findings.[6,7]

3,3-Bis(nitromethyl)oxetane (II) in 0·1M 85% ethanolic sodium hydroxide solution (Table 1), unlike other primary and secondary mono or α,ω-bisnitronate anions in solution which have been examined,[8–12] shows two strongly absorbing bands (λ_{max} 246, 257 mμ) of nearly equal intensity rather than the single band usually found near 237 ± 10 mμ.[12] However, at low hydroxide ion concentration ($1{\cdot}5 \times 10^{-4}$ M; molar ratio of base to compound = ca. 2·4:1) the band at 257 mμ disappears, only the band at 246 mμ being apparent (lower absorption intensity). At the intermediate base concentration of 0·001M one observes the 246 mμ band with a shoulder near 257 mμ. These observations suggest assignment of the 246 mμ band to the mononitronate anion (IV) and the 257 mμ band to the bisnitronate anion (V). The high intensity of the absorption (ε_{max}ca. 19,000) in 0·1M sodium hydroxide solution suggests a high concentration of bisnitronate anion.



(1)

IV, λ_{max} 246 mμ   V, λ_{max} 257 mμ

$$O_2NCH_2CH_2CH{=}NO_2^- \underset{}{\overset{OH^-}{\rightleftharpoons}} {}^-O_2N{=}CHCH_2CH{=}NO_2^- \qquad (2)$$

VI, λ_{max} 238 mμ   VII, λ_{max} 247 mμ

The above data may be compared with spectra of other primary α,ω-bis-nitronate anions in 85% ethanolic sodium hydroxide solution (Table 1). 1,3-Dinitropropane forms a bisnitronate anion (VII) (λ_{max} 247 mμ) and mononitronate anion (VI) (λ_{max} 238 mμ), depending on the concentration of base. In 1,6-dinitrohexane the bis and mononitronate anions absorb at nearly the same wavelength (238·5 and 238 mμ, respectively), similar to propane-1-nitronate (237 mμ); the 1,4- and 1,5- isomers have intermediate values of λ_{max} for the bis-nitronate anions.[11] The 9–11 mμ bathochromic shift observed in forming the 1,3-bisnitronate anions V and VII from the mononitronate anions IV and VI may be attributed to the electron withdrawing inductive effect of the carbonitronate group ($CH{=}NO_2^-$) in the β position, stabilizing the excited

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[6] A. T. Nielsen, *J. Org. Chem.* **27**, 1998 (1962).

[7] E. Schmidt, A. Ascherl and L. Mayer, *Ber. Dtsch. Chem. Ges.* **58**, 2430 (1925).

[8] M. F. Hawthorne, *J. Amer. Chem. Soc.* **79**, 2510 (1957); measurements in 80% ethanol.

[9] A. T. Nielsen, *Chem. & Ind.* 1358 (1957).

[10] A. T. Nielsen, *J. Org. Chem.* **27**, 2001 (1962).

[11] A. T. Nielsen and H. F. Cordes, *Tetrahedron* **20**, Suppl. 1, 235 (1964).

[12] F. T. Williams, Jr., Pat W. K. Flanagan, W. J. Taylor and H. Shechter, *J. Org. Chem.* **30**, 2674 (1965); measurements in water (absorption max shifted hypsochromically ca. 5 mμ relative to values in 85% EtOH).

state.[12] A phenyl group in the β position (2-phenylethane-1-nitronate) produces a 4·5 mμ shift (λ_{max} 241·5 mμ) relative to propane-1-nitronate anion with a methyl group in the β position.

TABLE 1. UV ABSORPTION SPECTRA OF PRIMARY NITRONATE ANIONS
(85% ethanolic sodium hydroxide solution)

Compound	Conc., M × 10^5	NaOH Conc., M	λ_{max} mμ	ε_{max}[a]
II	6·4	0·1	246	19,400[b]
			257	18,900[b]
	6·4	0·01	246	15,800
			257	16,000
	6·4	0·001	246	6600
			257 (sh)	5700
	6·4	0·00015	246	4100
$(CH_3)_2C(CH_2NO_2)_2$	0·71	0·1	238·5	12,700[c]
	6·4	0·01	238·5	12,700[c]
	6·4	0·00015	238	2900
$O_2N(CH_2)_3NO_2$	10	0·01	247	16,600[d]
	10	0·00015	238	5000
$O_2N(CH_2)_6NO_2$	7·4	0·01	238·5	21,200[c]
	7·4	0·00015	238	6480[c]
$CH_3CH_2CH_2NO_2$	10	0·01	237	10,200[c]
	10	0·00015	237·5	2000[c]
$C_6H_5CH_2CH_2NO_2$[e]	12·4	0·01	241·5	11,200[c]

[a] Max values obtained.

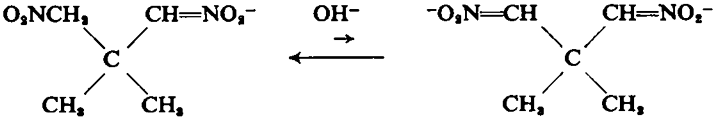
[b] Values obtained after 1 hr reaction; ε_{max} reduced by ca. one-half after standing 18 hr.

[c] No significant change of value with time. 2,2-Dimethyl-1,3-dinitropropane was prepared by the procedure of A. Lambert and A. Lowe [*J. Chem. Soc.* 1517 (1947)] and recrystallized from EtOH, m.p. 87–89°. H. B. Fraser and G. A. R. Kon [*J. Chem. Soc.* 604 (1934)] report m.p. 89–90°.

[d] Value obtained after 4 min; ε_{max} decreases rapidly with time.[10]

[e] The 2-phenyl-1-nitroethane employed was a generous gift of Professor N. Kornblum.

The equilibrium between oxetane mononitronate (IV) and bisnitronate (V) anions (Eq 1) appears to favor less bisnitronate than the equilibrium between the unsubstituted ions VI and VII (Eq. 2) ($K_{eq}^2 > K_{eq}^1$) as suggested by the appearance of absorption bands of both IV and V even in 0·1M sodium hydroxide solution. Also, a slower rate of nitronate ion formation was observed for II relative to 1,3-dinitropropane. The neopentyl-like structure of 3,3-bis(nitromethyl)oxetane is probably responsible for these effects. Hindrance to solvation and/or electrostatic repulsion of *gem* carbonitronate groups in the bisnitronate anion (V) disfavor its formation. An extreme example of this phenomenon is found in dinitroneopentane which forms principally mononitronate anion (VIII) (λ_{max} 238·5 mμ, ε_{max} 12,700) in 0·1M 85% ethanolic sodium hydroxide solution (Eq. 3). The low values of both λ_{max} and ε_{max} suggest the presence of only very small amounts of bisnitronate anion (IX) (expected λ_{max} ca. 247 mμ, ε_{max} ca. 20,000 for a 1,3-bisnitronate anion); $K_{eq}^3 < K_{eq}^1$. The absorption maximum (238·5 mμ) is in agreement with that of alkyl substituted primary mononitronate anions (235–240 mμ, solvent corrected to 85% ethanol).[12] Also the absorption maximum (238·5 mμ) is unchanged over a very wide range of base concentration (Table 1).



(3)

VIII, λ_{max} 238·5 mμ   IX

The slow dextruction of II in basic solution (in contrast to the stability of dinitroneopentane) as evidenced by the lowering of the extinction coefficient suggests the the possibility of basic cleavage of the oxetane ring; this degradation reaction was not examined, however. The marked instability, in basic solution, of 1,3-dinitroalkanes lacking substituents in the 2-position has been studied.[10] All nitronate anions examined, including the least stable propane-1,3-bisnitronate, can, when promptly acidified, are reconverted (*via* the intermediate nitronic acids) to the parent nitroalkane; the mechanism of this process has been studied.[11]

The value of the absorption maximum of the oxetane mononitronate anion IV (246 mμ) is somewhat high for a primary mononitronate ion (expected, ca. 238 mμ). The bathochromic shift observed (8 mμ) may be attributed to the inductive effect of the adjacent oxetane ring. The unusually high value of the maximum of the oxetane bisnitronate anion (257 mμ) thus results from the combined electron withdrawing effects of the oxetane ring and the β-carbonitronate group, both of which stabilize the excited state ($\lambda_{max} = 238 + 8 + 10 = 256$ mμ). Like carboxylate, the carbonitronate group is a fair electron attractor.

The somewhat exalted electronegative nature of the oxetane ring has been discussed and is evident from many observations;[1] however, no satisfactory theoretical explanation for the effect has yet been offered. The remarkable ease of halide displacement from 3,3-bis(halomethyl)oxetanes may be attributed in part to this property.[1,2] The UV spectra observed in the present work also appear to illustrate the phenomenon. The bathochromic shift produced by the oxetane ring (ca. 8 mμ) is slightly greater than that of its lower homolog, oxirane[13,14] (6 mμ). On the other hand, in the carbocyclic series the order is reversed; the well known conjugative effect of cyclopropyl produces a marked bathochromic shift (10–15 mμ)[12–15] relative to cyclobutyl (ca. 7 mμ);[12] cf. cyclopropylmethanenitronate, λ_{max} 242·5 mμ, and propane-1-nitronate, λ_{max} 231·5 mμ in water;[12] 1-cyclopropylethane-1-nitronate, λ_{max} 240 mμ, and propane-1-nitronate λ_{max} 227 mμ, in 80% ethanol.[8]

Unsuccessful attempts were made to prepare 3,3-bis(nitromethyl)oxetane (II) by other procedures. The 3,3-bis(halomethyl)oxetanes readily undergo nucleophilic displacement reactions leading to 3,3-disubstituted oxetanes[1,2] with anions such as iodide,[16] cyanide,[17] acetate,[18] ethoxide,[18] phenoxide,[16] thiophenoxide[16] and azide.[19] However, 3,3-bis(bromomethyl)oxetane failed to produce II by reaction with sodium

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[16] T. W. Campbell, *J. Org. Chem.* **22**, 1029 (1957).

[17] S. Searles, Jr. and E. F. Lutz, *J. Amer. Chem. Soc.* **81**, 3674 (1959).

[18] A. C. Farthing, *J. Chem. Soc.* 3648 (1955).

[19] W. R. Carpenter, *J. Org. Chem.* **27**, 2085 (1962).

nitrite in dimethylformamide;[20] this result might have been predicted from the known difficulty of preparing nitroalkanes having electron withdrawing groups by this method.[21] No II was obtained by reaction of 3,3-bis(bromomethyl)oxetane with silver nitrite under conditions whereby I produced II. No 3,3-bis(nitromethyl)oxetane (II) was produced by reaction of the bis-4-toluenesulfonate ester of 3,3-bis-(hydroxymethyl)oxetane (X) with sodium nitrite in dimethyl sulfoxide by known procedures.[20] Improved procedures for preparing glycol X and its diacetate (XI) from 3,3-bis(chloromethyl)oxetane (XII)[22–24] are described in the experimental part. Reaction of XII in dimethylformamide with one mole-equivalent of potassium acetate, followed by methanolysis, produced X and 3-chloromethyl-3-hydroxymethyloxetane, characterized as its hexafluoroacetone spiro ketal derivative.

EXPERIMENTAL[25]

3,3-*Bis(iodomethyl)oxetane* (I). A mixture of 38·8 g (0·25 mole) 3,3-bis(chloromethyl)oxetane,[22] 112·5 g (0·75 mole) NaI and 250 ml dry acetonitrile was heated under reflux with stirring for 10 hr. Working up in the usual manner gave 75·3 g (89%) I, m.p. 49°; reported m.p. 50°[16] 49°,[26] 47–48°.[27] The previously reported procedure,[16] employing 2-butanone solvent and a reflux time of 24 hr, produced an 89% yield of I, m.p. 50°.

3,3-*Bis(nitromethyl)oxetane* (II). A mixture of I (6·76 g; 0·02 mole), $AgNO_2$ (7·7 g; 0·05 mole) and 250 ml dry ether was stirred for 4 hr at 22° and then heated under reflux with stirring for 22 hr. The Ag-salts were removed by filtration and the filtrate concentrated to remove ether. The oily residue (4·9 g) was triturated with ice-cold EtOH to yield 0·42 g crystals, m.p. 75–125°. Two recrystallizations from EtOH gave chunky prisms, 0·10 g (3%), m.p. 145–146·5°; a third recrystallization gave long needles, m.p. 147–148°; ν cm^{-1} (Nujol mull) 1540 and 1370 (NO_2), 983 (C—O); absorption near 3500 and between 1540–2700 cm^{-1} absent. In a parallel experiment employing refluxing acetonitrile solvent (22 hr) no VII could be isolated. (Found: C, 34·05; H, 4·47; N, 15·34. $C_5H_8N_2O_5$ requires: C, 34·09; H, 4·58; N, 15·91%.)

3,3-Bis(bromomethyl)oxetane[28] in ether, stirred with $AgNO_2$ at room temp for 90 hr, gave no reaction, the reactants being completely recovered. Its reaction at room temp with $NaNO_2$ in dimethylformamide or with $NaNO_2$ in dimethyl sulfoxide,[20,21] failed to produce II.

3,3-*Bis(aminomethyl)oxetane* (III). A 16·5 mg sample of II in 10 ml acetic acid was stirred in a H_2 atm with Adams catalyst (700 mm, 25°)[6] and H_2 (4 mole-equivs) were absorbed in 1·5 hr after which time ca. 2 mole-equivs were slowly absorbed (15 hr). The mixture was filtered and the filtrate concentrated to yield crystals of III-diacetate which was converted into the dipicrate derivative of III; yellow prisms from EtOH, m.p. 246–249° (dec). When mixed with an authentic sample, m.p. 247–250° (dec), the m.p. was not depressed (reported[5] m.p. 237°). (Found: C, 36·43; H, 3·60; N, 18·51. $C_{17}H_{18}N_8O_{15}$.0·5 C_2H_5OH requires: C, 36·18; H, 3·54; N, 18·75%.)

The authentic sample of III was prepared from I by reaction with aqueous ethanolic ammonia at room temp; it has been prepared previously from 3,3-bis(bromomethyl)oxetane[5] or 3,3-bis(chloromethyl)oxetane[16] by reaction with ammonia.

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[20] N. Kornblum, H. O. Larson, R. K. Blackwood, D. D. Mooberry, E. P. Oliveto and G. E. Graham, *J. Amer. Chem. Soc.* **78**, 1497 (1956).

[21] N. Kornblum, *Organic Reactions* **12**, 113 (1962).

[22] We are grateful for a generous sample of 3,3-bis(chloromethyl)oxetane provided by the Hercules Powder Company.

[23] F. Govaert and M. Beyaert, *Proc. Acad. Sci. Amsterdam* **42**, 790 (1939); *Chem. Abstr.* **34**, 5415 (1940).

[24] C. H. Issidorides and A. I. Matar, *J. Amer. Chem. Soc.* **77**, 6382 (1955).

[25] UV spectra were determined with a Cary recording spectrophotometer, Model 11MS.

[26] F. Govaert and M. Beyaert, *Natuurw. Tijdschr.* **22**, 73 (1940); *Chem. Abstr.* **37**, 3054 (1943).

[27] S. Kambara and M. Hatano, *Kogyo Kagaku Zasshi* **61**, 904 (1958); *Chem. Abstr.* **55**, 18696 (1961).

[28] 3,3-Bis(bromomethyl)oxetane was prepared in 72% yield from tris(bromomethyl)ethyl acetate by reaction with MeONa in MeOH (1 hr reflux).[16]

3,3-*Bis(acetoxymethyl)oxetane* (XI). A mixture of 77·5 g (0·5 mole) of XII,[22] potassium acetate (150 g; 1·5 moles, dried at 110° for 24 hr), and 400 ml dry, freshly distilled dimethylformamide was heated, with stirring, at 120–130° for 6 hr. The solution was cooled to 25° and the precipitated salts removed by filtration and washed with 100 ml dimethylformamide. The combined filtrates were evaporated at 20 mm (steam bath) to leave an oily residue; this was dissolved in 250 ml CH_2Cl_2, filtered to remove additional salts and the filtrate concentrated. Distillation of the residue gave 96·0 g (95%) of XI, b.p. 83–84° (0·4 mm); reported[24] b.p. 85–87° (1 mm).

3,3-*Bis(hydroxymethyl)oxetane* (X). The oily residue of XI from a run identical to that above was dissolved in 250 ml MeOH; 0·5 g MeONa was added and the solution heated under reflux for 3 hr, the methyl acetate being distilled as formed. After neutralizing the catalyst with HCl (*p*H 7), the MeOH was distilled and the residue distilled to yield 51 g (87% from XII) of X, b.p. 125–127° (0·4 mm); reported b.p. 128° (0·4 mm);[23] 135–138° (1–2 mm).[24]

3-*Chloromethyl*-3-*hydroxymethyloxetane*. Compound XII (155 g; 1·0 mole), 98 g (1·0 mole) anhydrous potassium acetate, and 250 ml dry dimethylformamide were heated at 125° for 8 hr. The solution was cooled, the precipitate of KCl removed by filtration, and the dimethylformamide stripped *in vacuo* by heating on the steam bath. The residue was dissolved in 250 ml MeOH, 1 g MeONa was added and the solution heated under reflux while the methyl acetate was distilled as formed. After the ester exchange reaction was complete the MeONa was neutralized with HCl and the excess MeOH removed by distillation. Distillation of the residue at 3 mm gave fractions: (1) b.p. <100°, 40·8 g, principally recovered XII; (2) b.p. 100–103° [reported b.p. 64° (0·09 mm),[16] 142–145° (4–5 mm),[29] 110–130° (4 mm)[30]], 47·5 g (35% conversion, 47% yield based on unrecovered XII) of 3-chloromethyl-3-hydroxymethyloxetane, (3) residue, 48·8 g, believed to be principally X.

7,7-*Bis(trifluoromethyl)*-2,6,8-*trioxaspiro*[3·5]*nonane*. A solution of 34·1 g (0·25 mole) 3-chloromethyl-3-hydroxymethyloxetane in 200 ml dry tetrahydrofuran was prepared in a 500 ml flask equipped with a sealed stirrer, dry ice–acetone cooled condenser and gas inlet tube. Hexafluoroacetone (41·5 g, 0·25 mole) was introduced and the temp controlled by ice bath cooling. The condenser was then replaced by an ice water-cooled condenser and NaH (6 g, 0·25 mole) added in portions with stirring during 3 hr, with occasional cooling to maintain the temp below 30°. The solution was then heated under reflux (reaction temp 68–69°) for 48 hr. After cooling, 10 ml MeOH was added to decompose a slight excess NaH and the solution poured into 500 ml cold water. The precipitate of 7,7-bis(trifluoromethyl)-2,6,8-trioxaspiro[3,5]nonane was removed by filtration, washed with ice water and dried. The crude product (40·0 g) was recrystallized from 150 ml hot benzene to yield 33·9 g (51%) colorless, transparent prisms, m.p. 125·5–126·5°. (Found: C, 36·24; H, 2·92; F, 42·54. $C_8H_8F_6O_3$ requires: C, 36·10; H, 3·03; F, 42·83%.)

3,3-*Bis(4-toluenesulfonoxymethyl)oxetane*. A mixture of 33·8 g (0·1 mole) of I, 56·0 g (0·20 mole) silver 4-toluenesulfonate and 200 ml dry acetonitrile (distilled from CaH_2) was heated under reflux with stirring for 12 hr. After cooling to ca. 50°, the precipitate of AgI was removed by filtration and washed with 50 ml hot acetonitrile. The combined filtrates deposited 23·4 g material; from the mother liquors, by concentration followed by crystallization from 2-propanol, an additional 16·1 g product was obtained; total yield 39·5 g (93%), m.p. 109–110°. Recrystallization from benzene gave 37·3 g 3,3-bis(4-toluenesulfonoxymethyl)oxetane, m.p. 109·5–110·5°. The bistosylate was also prepared in 5% yield from X by reaction with 4-toluenesulfonyl chloride in pyridine; m.p. 108–109°, after recrystallization from EtOH. (Found: C, 53·47; H, 5·55; S, 14·88. $C_{19}H_{22}O_7S_2$ requires: C, 53·50; H, 5·20; S, 15·04%.)

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[30] R. Koehler and H. Pietsch, British Pat. 797,276 (1958); *Chem. Abstr.* **53**, 767 (1959).