171. J. G. Niedzwicki, M. H. Iltzsch, M. H. El Kouni, and S. Cha, Biochem. Pharmacol., 33, 2383 (1984).
172. C. Wasternack, H. Reinbothe, and E. Golovinsky, Dokl. Bolg. Akad. Nauk, 31, 469 (1978).
173. O. Fliegerova, H. Skodova, J. Farkas, and J. Skoda, Coll. Czech. Chem. Commun., 41, 2073 (1976).
174. Kaken Chemical Co., Ltd., Japanese Patent No. 80160775; Chem. Abstr., 95, 25540 (1981).
175. Kaken Chemical Co., Ltd., Japanese Patent No. 81152476; Chem. Abstr., 96, 123235 (1982).
176. P. C. Srivastava and R. K. Robins, J. Med. Chem., 24, 1172 (1981).
177. Sankyo Co., Ltd., Japanese Patent No. 8235515; Chem. Abstr., 97, 150,761 (1982).
178. G. Jäeger, H. Hagemann, K. Findeisen, A. Von Koenig, A. L. Poot, and J. F. Von Besauw, German Öffen. No. 2520956; Chem. Abstr., 87, 76381 (1977).

1,3-DIPOLAR CYCLOADDITION OF 2-BENZYLIDENEINDAN-1,3-DIONE α-OXIDE TO OLEFINS

M. Yu. Krysin, I. K. Anokhina, and L. P. Zalukaev

UDC 547.442.3'572.3'712.2'728.04

A carbonyl ylid, which reacts with maleic anhydride, N-phenylmaleinimide, and β-nitrostyrene to form adducts resulting from 1,3-dipolar cycloaddition, is formed reversibly when 2-benzylideneindan-1,3-dione α-oxide is heated (80°C). The reaction proceeds regio- and stereospecifically.

We have investigated the ability of 2-benzylideneindan-1,3-dione α-oxide (I) to undergo a thermal 1,3-dipolar cycloaddition reaction. We were compelled to do this because of the relatively little study devoted to the thermal transformations of epoxy ketones; at the same time, a significant amount of research has been devoted to their photochemistry [1-3]. Moreover, 1,3-dipolar cycloaddition reactions with the participation of spirooxiranes have not been studied at all. Only the generation of carbonyl ylids from oxopyrazonespirooxiranes has been described [4, 5]. It also seemed of interest to examine the regio- and stereochemical peculiarities of the cycloaddition.

It is well known that the activity of addends in 1,2-dipolar cycloaddition reactions depends mainly on their donor-acceptor properties [6]. We selected β,β-dimethylstyrene, cyclohexene, and 1-heptene as olefins with increased nucleophilicity of the double bond and maleic acid derivatives (the anhydride, N-phenylimide, and dimethyl ester), methyl methacrylate, vinyl acetate, β-nitrostyrene, trans-stilbene, and trans-4,4'-dinitrostilbene as alkenes with increased electrophilicity of the double bond. An analysis of the reactivities of these dipolarophiles enabled us to draw a conclusion regarding the character of the interaction of the boundary orbitals of the reagents. We used benzene or liquid dipolarophiles as the solvents.

The formation of cycloaddition products was not detected from TLC and PMR spectroscopic data in the reactions of α-oxide I with dimethylstyrene, cyclohexene, and 1-heptene (see scheme on following page).

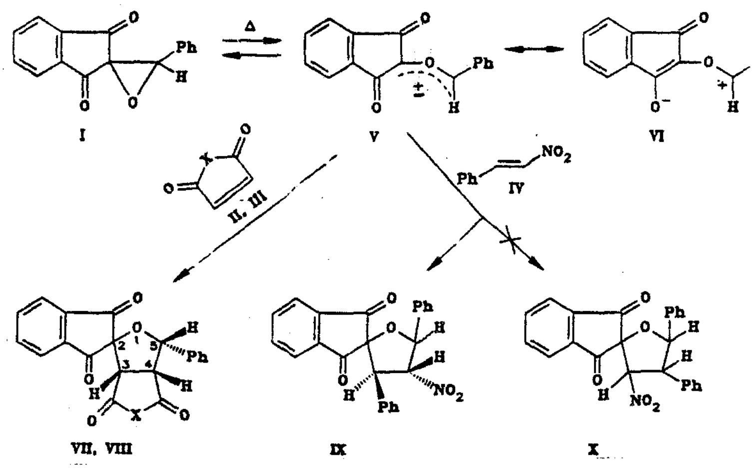
Olefins with reduced electron density of the C=C bond displayed different reactivities. The cycloaddition adducts were obtained only for anhydride II and imide III of maleic acid and nitrostyrene IV. Methyl methacrylate and vinyl acetate underwent polymerization under the reaction conditions. Cycloaddition products were not isolated for the remaining dipolarophiles.

Only one of the possible isomers was isolated in 50-70% yield from the reaction mixture for dipolarophiles II-IV. The residue after isolation of the desired product was a resinous

---

Lenin Komsomol Voronezh State University, Voronezh 394696. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1463-1466, November, 1987. Original article submitted March 5, 1986.

0009-3122/87/2311-1166$12.50



mass with a complex composition, the separation of which was impossible by column chromatography.

A characteristic doublet of vibrations of carbonyl groups of an indandionyl ring was observed in the IR spectra of adducts VII-IX (Table 1), i.e., the carbonyl ylid reacted in the 1,3-dipole form V rather than in the 1,5-dipole form VI [7]. In the PMR spectra the signal of the 5-H proton is found at 6 ppm [8]. The assignment of the signals of the 3- and 5-H protons was made by means of double homonuclear resonance with decoupling of the 5-H proton. An uncertainty due to the conformational inhomogeneity of the rings (a very small barrier to interconversions of the conformations) arises in attempts to use the vicinal spin-spin coupling constants (SSCC) for configurational assignments in series of cyclopentane and/or tetrahydrofuran derivatives [9]. It is therefore impossible, even for the experimentally found ^3J constants, to establish the stereochemistry of the substituents in five-membered rings on the basis of these constants.

We suggest that the most likely structures for adducts VII and VIII will be those presented in the scheme. This is due, first of all, to the fact that the most favorable configuration for carbonyl ylid V will be that with an exo orientation of the phenyl group [7, 10] and, second, to the endo character of cycloaddition [11].

The regiochemistry of the addition of nitrostyrene IV was established exclusively on the basis of PMR spectroscopic data. Let us examine two possible structures of the adduct, IX and X. The signals of the 3-H proton in IX and the 4-H proton in X will be found at

TABLE 1. Properties of the Adducts of 2-Benzylideneindan-1,3-dione with Olefins

Compound	m/z	ν, cm⁻¹	δ, ppm	Found, %			Empirical formula	Calc., %			Yield, %
				C	H	N		C	H	N	
VII	348	1704 1743 1777 1853	60 MHz (d_6-acetone): 4,32 (d, 1H, 8,5 Hz, 3-H); 4,59 (dd, 1H, 7,0 Hz, 8,5 Hz, 4-H); 6,13 (d, 1H, 7,0 Hz, 5-H); 7,20—7,45 (m, 5H, arom); 8,04 (s, 4H, arom)	70,1	3,7		$C_{20}H_{12}O_6$	68,9	3,5		51
VIII	423	1379 1712 1740 1768	100 MHz (DMSO-D_6): 4,13 (d, 1H, 8,2 Hz, 3-H); 4,24 (dd 1H, 6,8 Hz, 8,2 Hz, 4-H); 6,05 (d, 1H, 6,8 Hz 5-H); 7,06—7,55 (m, 10H. arom.); 8,08 (s, 4H, arom.)	73,7	3,9	3,6	$C_{26}H_{17}NO_5$	73,7	4,0	3,3	73
IX	399	1350 1552 1718 1751	60 MHz ($CDCl_3$): 4,90 (d, 1H, 10,0 Hz, 3-H); 6,18 (d, 1H, 9,0 Hz, 5-H); 6,50 (dd, 1H, 9,0 Hz 10,0 Hz, 4-H); 7,00—7,90 (m, 14H, arom.)	71,9	4,3	3,5	$C_{24}H_{17}NO_5$	72,2	4,3	3,5	58

stronger field; however, their multiplicities will differ. The PMR spectra of the adduct of α-oxide I and nitrostyrene IV contains a doublet at 4.90 ppm (J = 10 Hz). This constitues absolutely unequivocal evidence in favor of structure IX. The assignment of the 4-H and 5-H signals was made by means of decoupling of the 3-H proton. For the reason indicated above, it is impossible to establish the orientation of the 5-H proton.

This sort of regiochemistry of the addition of unsymmetrical ylid V is in agreement with theoretical predictions on the basis of highest occupied molecular orbital (HOMO)—lowest vacant molecular orbital (LVMO) interactions [12]. The carbon atom of the indandionyl fragment will be the most nucleophilic part of the 1,3-dipole. Addition of the most electrophilic part of the β-nitrostyrene molecule — the carbon atom in the α position relative to the phenyl ring — takes place precisely at this atom.

The experimentally found character of the reactivities of dipolarophiles with the C=C bond shows that cycloaddition with the participation of ylid V is controlled by interaction of the HOMO of the dipole with the LVMO of the dipolarophile, i.e., it corresponds to "type I" in accordance with the Sustmann classification [13].

Thus it was established that, under mild conditions, spiro epoxy ketone I generates carbonyl ylid V, which undergoes 1,3-dipolar cycloaddition with the most electron-deficient olefins: maleic acid anhydride and N-phenylimide and β-nitrostyrene. The process is regio- and stereospecific.

EXPERIMENTAL

The IR spectra were recorded with Specord (KBr pellets) and UR-20 (suspensions in mineral oil) spectrometers. The PMR spectra were obtained with Varian-100 and Tesla BS-467 spectrometers.* The mass spectra were recorded with a Hewlett-Packard 5985 spectrometer. Thin-layer chromatography was carried out on Silufol UV-254 plates by elution with chloroform—ethyl acetate (20:1).

General Method for Carrying Out the Cycloaddition. A mixture of 0.5 g (2 mmole) of α-oxide I [14] and 2.0-2.1 mmole of the dipolarophile was refluxed in 15-20 ml of absolute benzene in an argon atmosphere until the spot of α-oxide I disappeared on the thin-layer chromatogram (15-30 h). The adducts were isolated by cooling the mixture. Another certain amount of the product was able to be obtained additionally from the mother liquor.

2-Phthaloyl-5-phenyltetrahydrofuran-3,4-dicarboxylic Acid Anhydride (VII). The reaction of 0.5 g of α-oxide I and 0.2 g of anhydride II gave 0.36 g of VII with mp 202-203.5°C (from ethyl acetate).

2-Phthaloyl-5-phenyltetrahydrofuran-3,4-dicarboxylic Acid N-Phenylimide (VIII). The reaction of 0.5 g of α-oxide I and 0.35 g of III [15] gave 0.62 g of adduct VIII with mp 285-286°C (from acetone).

4-Nitro-2-phthaloyl-3,5-diphenyltetrahydrofuran (IX). The reaction of 0.5 g of α-oxide I and 0.31 g of nitrostyrene IV gave 0.46 g of IX with mp 189-190°C (from benzene).

LITERATURE CITED

1. S. Bodforss, Chem. Ber., 51, 214 (1918).
2. E. F. Ullmann and J. E. Milks, J. Am. Chem. Soc., 86, 3814 (1964).
3. H. Kato, H. Tezuka, K. Yamaguchi, K. Nowada, and Y. Nakamura, J. Chem. Soc., Perkin Trans. 1, No. 9, 1029 (1978).
4. S. N. Ege, A. D. Adams, E. J. Gess, K. S. Ragone, B. J. Kober, M. B. Lampert, P. Umrigar, D. C. Lankin, and G. W. Griffin, J. Chem. Soc., Perkin Trans. 1, No. 2, 325 (1983).
5. P. Umrigar, G. W. Griffin, B. A. Lindig, F. M. Anne, P. K. Das, T. S. Leslie, A. M. Trozzolo, S. N. Ege, and A. Thomas, J. Photochem., 22, 71 (1983).
6. Ya. D. Samuilov and A. I. Konovalov, Usp. Khim., 53, 566 (1984).
7. C. V. Kumar, D. Ramajah, P. K. Das, and M. V. George, J. Org. Chem., 50, 2818 (1985).
8. J. Brokatzky-Geiger and W. Eberbach, Heterocycles, 16, 1907 (1981).

---

*We thank S. I. Kolbasenko and A. G. Kutateladze for their assistance in recording the PMR spectra.

9. E. Eliel, N. Allinger, S. Angyal, and G. Morrison (eds.), Conformational Analysis, Wiley-Interscience, New York (1965).
10. T. Do-Minh, A. M. Trozzolo, and G. W. Griffin, J. Am. Chem. Soc., 92, 1402 (1970).
11. K. N. Houk, J. Sims, C. R. Watts, and L. J. Luskus, J. Am. Chem. Soc., 95, 7301 (1973).
12. K. N. Houk, N. G. Rondan, C. Santiago, R. J. Gallo, R. W. Gandour, and G. W. Griffin, J. Am. Chem. Soc., 102, 1504 (1980).
13. R. Sustmann, Tetrahedron Lett., No. 29, 2717 (1971).
14. W. Leimgruber and M. Weigele, US Patent No. 3832362; Ref. Zh. Khim., 12N197P (1975).
15. M. P. Cava, A. A. Deana, K. Muth, and M. Meigel, in: Organic Syntheses, Vol. 12, A. Blatt (ed.), Wiley, New York (1943).

REACTIONS OF ACETOPHENONES AND BORON TRIFLUORIDE ETHERATE IN THE PRESENCE OF HOMOLOGS OF ORTHOFORMIC ESTER

I. I. Boiko, M. É. Dergunova, and T. N. Boiko

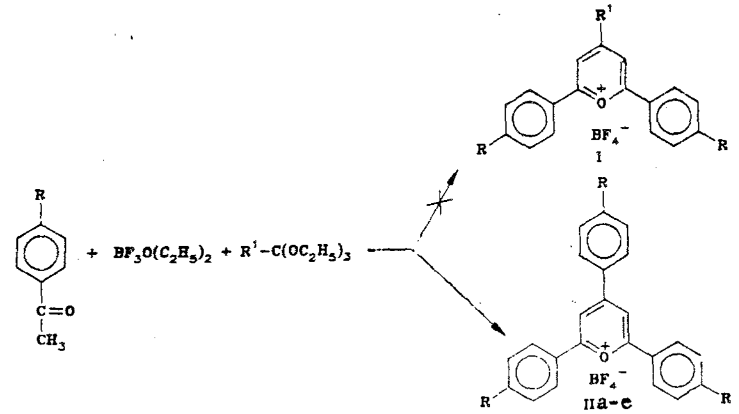
UDC 547.166'127.3'572.1'812.5.07

It was established that homologs of orthoformic ester (orthoacetic and orthopropionic esters), in contrast to it, do not undergo reaction with substituted acetophenones and boron trifluoride etherate to give γ-alkylpyrylium salts; the products obtained are 2,4,6-triarylpyrylium tetrafluoroborates.

It is known that pyrylium salts with an active methyl group are starting compounds for the synthesis of a number of polymethine dyes. The preparation of 2,6-diarylpyrylium tetrafluoroborates [1] via the Dorofeenko–Mezheritskii reaction [2] from substituted acetophenones, orthoformic ester, and boron trifluoride etherate, has been described in the literature.

In the present research we set out to ascertain the possibility of the use of homologs of orthoformic ester in the Dorofeenko–Mezheritskii reaction for obtaining pyrylium tetrafluoroborates I with an active methyl or methylene group in the 4 position of the pyrylium ring.

A mixture of the corresponding substituted acetophenone, orthoacetic or orthopropionic ester, and boron trifluoride etherate was heated for 1 h on a boiling-water bath. At the end of the process, from the reaction mass, by the usual methods, we isolated crystalline reaction products which, on the basis of the IR spectral data, can be classified as pyrylium salts. However, the PMR spectra indicated the absence of a methyl group in the pyrylium



Pereslavl Branch, All-Union State Scientific-Research and Planning Institute of the Photographic-Chemical Industry, Pereslavl-Zelesskii 152140. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1467-1469, November, 1987. Original article submitted March 26, 1986; revision submitted September 9, 1986.

0009-3122/87/2311-1169$12.50